FUEL CELL

RESEARCH & DEVELOPMENT

SATURATED HYDROCARBON FUEL CELL PROGRAM

TECHNICAL SUMMARY REPORT NUMBER 3
PART 1 - TASK IV
JANUARY 1, 1963 - JUNE 30, 1963
PROJECT SCIENTISTS: DRS. E. J. CAIRNS AND A. D. TEVEBAUGH

CONTRACT NUMBER DA 44-009-ENG-4909
ARPA ORDER NUMBER 247
PROJECT NUMBER 8A72-13-001-506

U.S. ARMY
ENGINEER RESEARCH AND DEVELOPMENT LABORATORIES
FT. BELVOIR, VIRGINIA

DIRECT ENERGY CONVERSION OPERATION

GENERAL ELECTRIC

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TECHNICAL ASSISTANTS: MR. D. C. BARTOSIK
MR. G. J. HOLM

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FOREWORD

This is Technical Summary Report Number 3 of a research program on Saturated Hydrocarbon Fuel Cells conducted by the General Electric Company under contract with the U.S. Army Engineer Research and Development Laboratories. The purpose of this program is to perform studies on the fuel electrode with emphasis on understanding the reactivity of LPG (e.g. propa. and butane) and with the goal of achieving equal or superior performance with liquid hydrocarbon. Work on this contract was initiated on Jan. 1, 1962. The work is divided into Part 1 and Part 2. Part 1 is being conducted at the General Electric Company Research Laboratory in Schenectady, New York, while Part 2 is being carried on at the Direct Energy Conversion Operation Fuel Cell Laboratory, General Electric Company, Lynn, Massachusetts. A detailed work statement of Parts 1 and 2 follows in the report.

Technical Summary Report Number 3 is issued in four sections according to the separate tasks. These technical summary reports are issued on a semi-annual basis; however, interim reports are issued when appropriate to cover a particular phase or area of investigation. The technical content of this report has been reviewed by ERDL prior to its publication. Close guidance and approval of work direction is given by Mr. B.C. Almaula of ERDL who has been appointed Contracting Officers Representative.

FOREWORD (Cont'd)

This work was made possible by the support of the Advanced Research
Projects Agency (Order No. 247) as a part of Project Loraine through
the U.S. Army Engineer Research & Development Laboratories,
Ft. Belvoir, Virginia under contract DA-44-009-ENG-4909.

To help facilitate an understanding of the order of the Tasks and the work of
the personnel involved in this series of reports as indicated in the Contract
Work Statement, a listing of the Tasks in Part 1 and Part 2 with the names
of the principal investigators is hereby included:

Part 1 - Hydrocarbon Anode Studies

Technical Direction:		Dr. H. A. Liebhafsky
Task I	- Principal Investigators:	Dr. D. W. McKee
		Dr. F. J. Norton
Task II	- Principal Investigator:	Dr. S. Gilman
Task III	- Principal Investigators:	Dr. W. T. Grubb
		Dr. L. W. Niedrach
	Technical Assistants:	Miss Carol Michalske
		Mr. Irwin B. Weinstock
Task IV	- Principal Investigators:	Dr. E. J. Cairns
		Dr. A. D. Tevebaugh
	Technical Assistants:	Mr. D. C. Bartosik
		Mr. G. J. Holm

Part 2 - Saturated Hydrocarbon Ambient Air Fuel Cell Development Program

Technical Direction:		Dr. E. A. Oster
Task I	- Principal Investigator:	Mr. David I. MacDonald
Task II	- Principal Investigator:	Mr. Harry J. Young
Task III	- Principal Investigators:	Dr. P. V. Popat
		Mr. Paul Chludzinski
		Mr. G. F. Wheeler

Saturated Hydrocarbon Fuel Cell Program

Contract Work Statement

(For the Year 1963)

Contract: U.S. Army Engineer Research & Development Laboratory
            DA-44-009-ENG-4909 (Modification 2&3)
            Effective date: 1 January 1963

The following is an excerpt from the Contract:

"The following new Item 1.a. is hereby added to and made a part of
Exhibit "A", Schedule of Work and Services:

1.   The Contractor shall for a period of twelve (12) months conduct
research on the fuel electrode with emphasis on understanding the re-
activity of LPG (e.g. Propane and Butane) and with the goal of achieving
equal or superior performance with liquid hydrocarbons. In addition the
Contractor shall attempt to extend the performance of the air electrod to
other CO_2-rejecting electrolytes that will permit operation at higher
temperatures without pressurization, e.g. to electrolytes exhibiting a
lower vapor pressure than that of sulphuric acid. This work shall be
fully integrated, but conducted in two parts as follows:

PART 1

Continue conducting fundamental research investigations on the fuel
anode and fuel cell systems where the constituents of liquified petroleum
gases (LPG) will receive major emphasis in fuel cells operating at higher
temperatures than those previously investigated. The principal objectives
are: (1) To further the understanding of fuel cells for saturated hydrocarbons
by investigating the adsorption, surface reactions, and electrode kinetics of
hydrocarbons and their oxygenated derivatives on catalysts and electro-
catalysts. (2) To advance the technology of fuel cells using saturated
hydrocarbons between 25 and 300°C.

Task I

ADSORPTION AND CATALYTIC DECOMPOSITION OF GASEOUS
HYDROCARBONS ON VARIOUS MATERIALS OF INTEREST AS POSSIBLE ANODES

1.   Previous techniques, suitably modified, shall be used to investigate
the kinetics of the cracking of propane and of simila- (and higher) hydro-
carbons (with particular attention to the formation of methane) on appropriate
metals in the range 100-200°C. The information so obtained will lead to a
better understanding of the mechanism of the cleavage of these molecules and
the electrochemical nature of the active sites where it occurs. The work shall
be extended to include interesting mixed fuels.

2. Similar experiments will be done on binary alloys and upon semi-conducting oxide films in the hope of inhibiting methane formation, it being understood that all materials investigated must be potentially useful as anodes in fuel cells.

Task II

ADSORPTION ON AND REACTIONS AT ANODES

The voltammetric techniques already developed will be applied to saturated hydrocarbons at higher temperatures. As a subsidiary activity, experiments on simpler molecules shall be carried out to the extent that they further the program objectives.

Task III

FUEL CELLS WITH ACIDIC ELECTROLYTES

1. Evaluation shall be made of the performance characteristics of complete fuel cells operating upon LPG constituents and related fuel molecules, when using metals of the platinum group as electrocatalysts. The effects of the following variables upon the rate and completeness of the electrochemical oxidation reaction will be investigated:

    a. Fuel structure
    b. Temperature
    c. Electrolyte composition
    d. Modification of the platinoid catalysts by alloying and other means
    e. Additives to the electrolyte phase and presence of intermediates therein
    f. Additives to the fuel gas phase, and presence of products therein

2. Galvanostatic measurements coupled with volumetric gas adsorption measurements and with product analysis shall be continued with greater emphasis on fuel cells under loaded conditions.

3. New electrode structures shall be investigated in the hope of finding types better suited to operation on the constituents of LPG.

4. A search for new electrocatalysts shall be undertaken with applicable results from Task I as guide.

Task IV

FUEL CELLS WITH NEW NON-ACID ELECTROLYTES

The following information shall be obtained on anodes and on fuel cells, with emphasis on the constituents of LPG:

a. Polarization curves and anode behavior
b. Material balances
c. Life data (as time permits)

PART 2

Conduct research investigations to develop a greater understanding of the chemical and physical phenomena associated with low temperature, high performance, liquid electrolyte fuel cells for operation on air and saturated hydrocarbon derived fuels. The work will be of a fundamental chemical engineering nature and directed toward defining the factors which characterize the ultimate limitations of this fuel cell and developing guidelines for further maximizing its performance.

Task I

Investigate, and, where necessary, synthesize carbon dioxide rejecting electrolytes suitable for union with air cathodes developed under Task II in batteries operating up to 300°C. These electrolytes will also be evaluated for their compatibility with possible anode systems known to have reactivity with selected saturated hydrocarbon fuels in this same temperature range.

Task II

With emphasis on the air cathode, develop the technology to make improved electrode structures using small amounts of dispersed platinum as a catalyst for use in fuel cells containing carbon dioxide rejecting electrolytes investigated in Task I and operating at temperatures up to 300°C.

Task III

Evaluate electrochemical cells for performance and life, operating with ambient air as the source of oxidant and components developed under Task I and II. Emphasis will be placed on determining heat and mass limitations imposed by practical cell operation, as well as the effect of airborne and electrolyte impurities resulting from electrode reactions on cell performance for cell temperatures up to 300°C."

I. SUMMARY

The objective of Task IV is the study of hydrocarbon fuel cells with non-acid electrolytes. In connection with this objective, new cell hardware has been designed and constructed, based on previous experience with organic fuels. High precision material balance equipment has been constructed, ard calibrations for the initial phases of the work have been completed.

As a first tage in the hydrocarbon work, the new equipment was tested on a well known system in order to prove the reliability of the apparatus and to test the usefulness of t~e off-specification lot of cesium carbonate purchased for this work. The second stage, that of establishing the performance of saturated hydrocarbons in the present system of platinum electrodes and cesium carbonate electrolyte, followed by suitable modifications for performance improvement, is now in progress.

II. INTRODUCTION

Most of the hydrocarbon fuel cell research presently being carried out has made use of strong acid electrolytes, because strongly basic solutions containing high concentrations of hydroxyl ion will react with the oxidation products of the hydrocarbon fuel, being consumed in the process. The strong acids, though they do reject CO_2, present corrosion problems, particularly when intermediate temperatures (100-$500^{\circ}C$) are used.

II. INTRODUCTION (Cont'd)

In the anticipation that non-acid electrolytes will present less severe corrosion problems, such systems are being investigated. The first electrolyte being considered seriously is cesium carbonate. Compared to strong acids and strong hydroxide solutions, the cesium carbonate presents very mild corrosion conditions. Probably the most important problem is that of the selection of suitable anode materials for high current density saturated hydrocarbon fuel cells. Platinum is expensive and is known to adsorb saturated hydrocarbons slowly and to a small extent in the presence of non-acid electrolytes (See previous reports in this series by L. W. Niedrach).

It is necessary that equipment suitable for testing electrode materials under a wide variety of operating conditions, and capable of performing material balances and gas analyses be available, in order to carry out an intelligent search for new anode electrocatalysts. The first phase of the work consisted of the design, construction, and testing of such equipment.

III. EQUIPMENT DESIGN AND CONSTRUCTION

On the basis of previous work with CH_3OH, it was established that material balances would be desirable in any evaluation of a hydrocarbon fuel cell system. This was achieved with CH_3OH (a liquid fuel), by use of a precision syringe drive;

<u>EQUIPMENT DESIGN AND CONSTRUCTION</u> (Cont'd)

however, the gaseous hydrocarbons introduce a more difficult problem

in accurate control and metering of very low (ca. 0.1 cc/min) gas flow

rates. This problem has been solved by the use of high accuracy

capillary-tube flowmeters with a dual-range manometer system. A low

volume, fast response fuel flow system necessary for accurate material

balance work has been completed and checked. The new cells incorporate

several new design features which eliminate previously encountered

problems such as loss of contact with reference electrodes (because of

bubbles), accumulation of bubbles, and ease of electrolyte water content

control. Improvements have also been made in the electrical measuring

equipment and chromatographic analysis techniques of fuel cell products.

a. Cell Design

The overall arrangement of the fuel cell, reference electrodes,

electrolyte traps and reservoir is shown in Figure 1. Figure 2 shows

an exploded view of the cell parts that were machined from Teflon.

Drawings of the individual cell parts are shown in Figures 3 through 8.

In the past, electrolyte samples could be taken, but only with

some inconvenience. The new design allows rapid sampling of the

electrolyte in the cell. This is achieved by the use of the two stop-

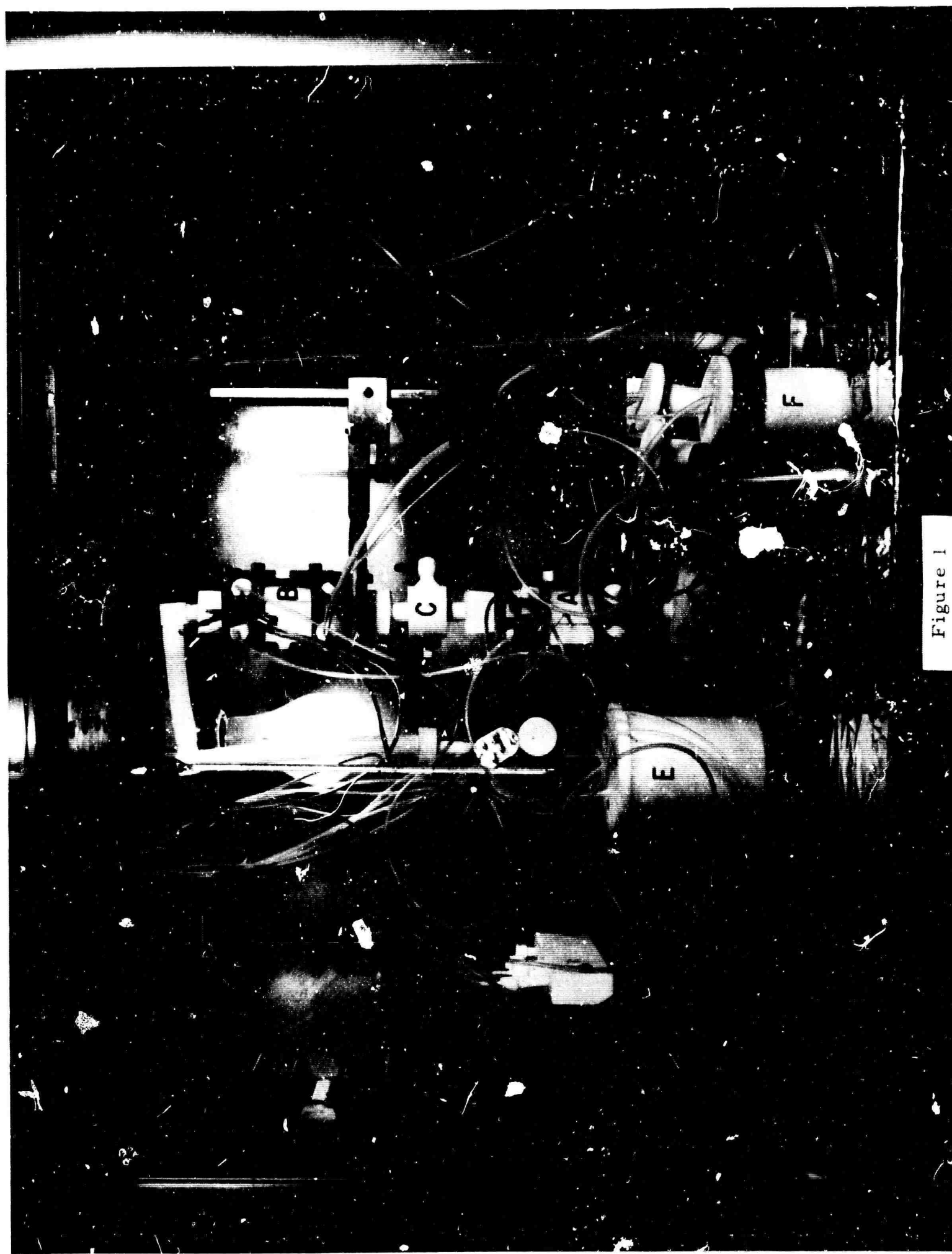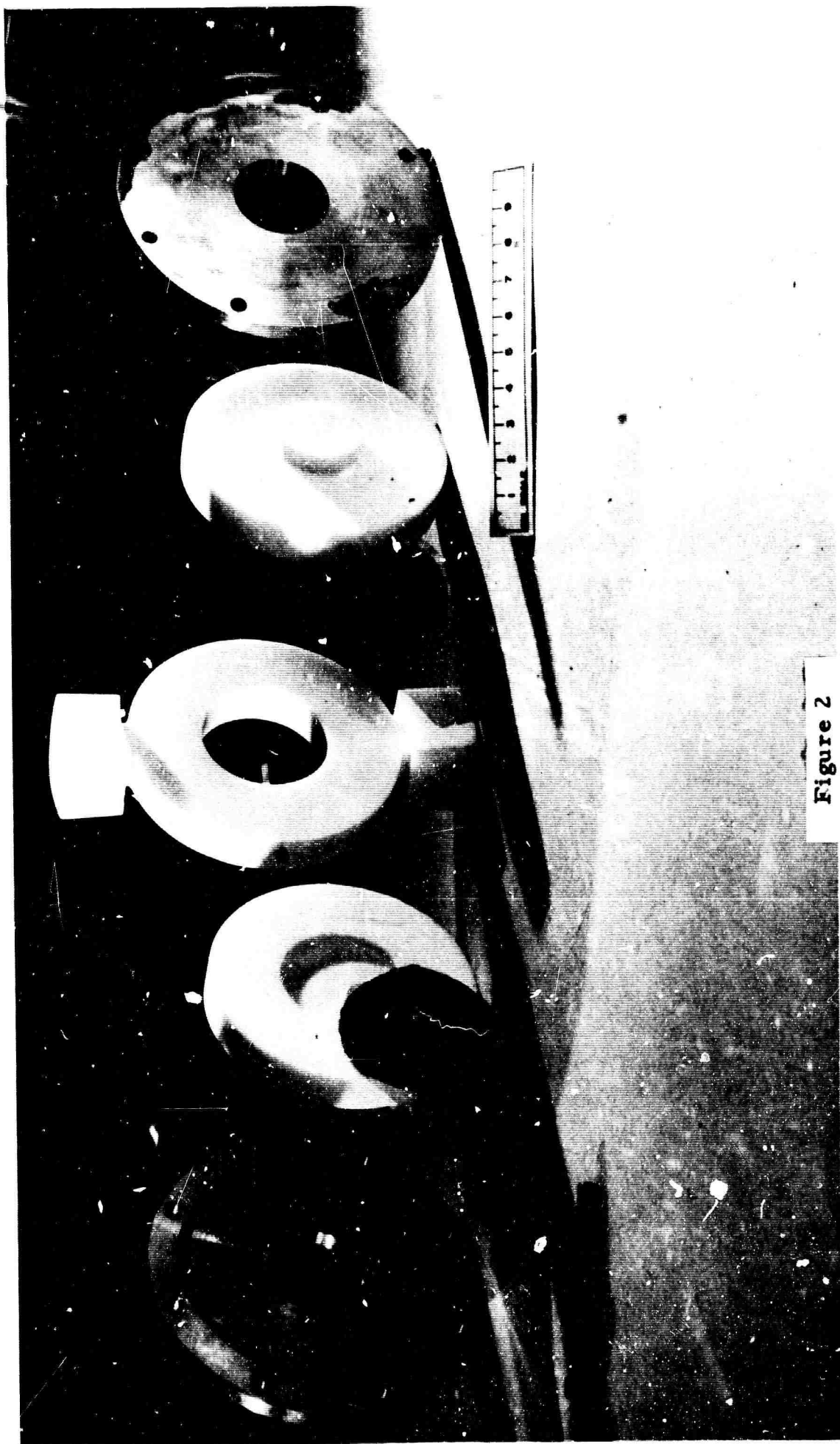cocks C and D shown in Figure 1.

Figure 1

Figure 2

-10-
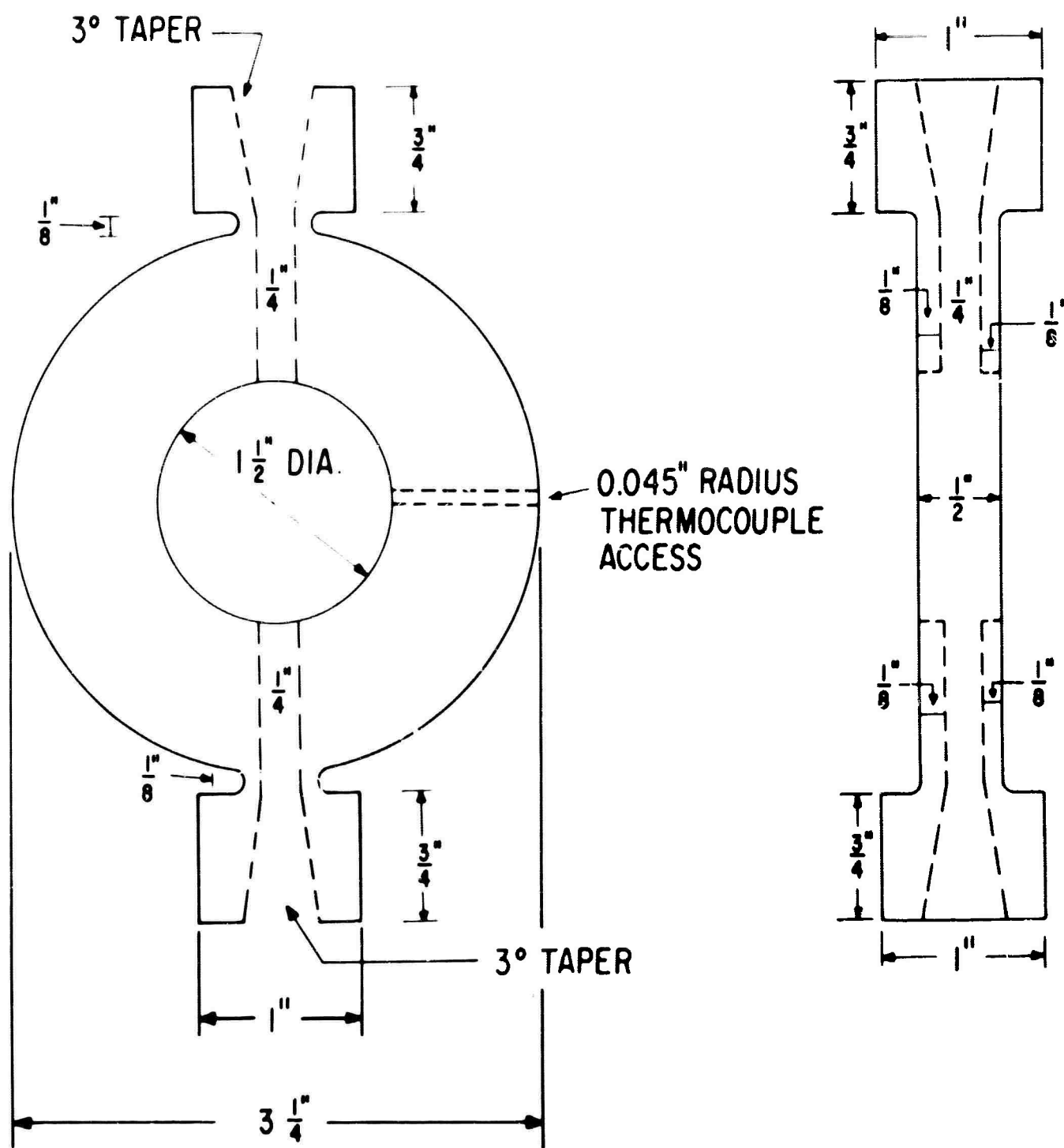
ELECTROLYTE CHAMBER

Figure 3

CELL END PLATES

Figure 4

END PLATES

4" DIA.

10-32 TAP

$1\frac{1}{8}$" DIA.

$3\frac{5}{8}$" DIA.
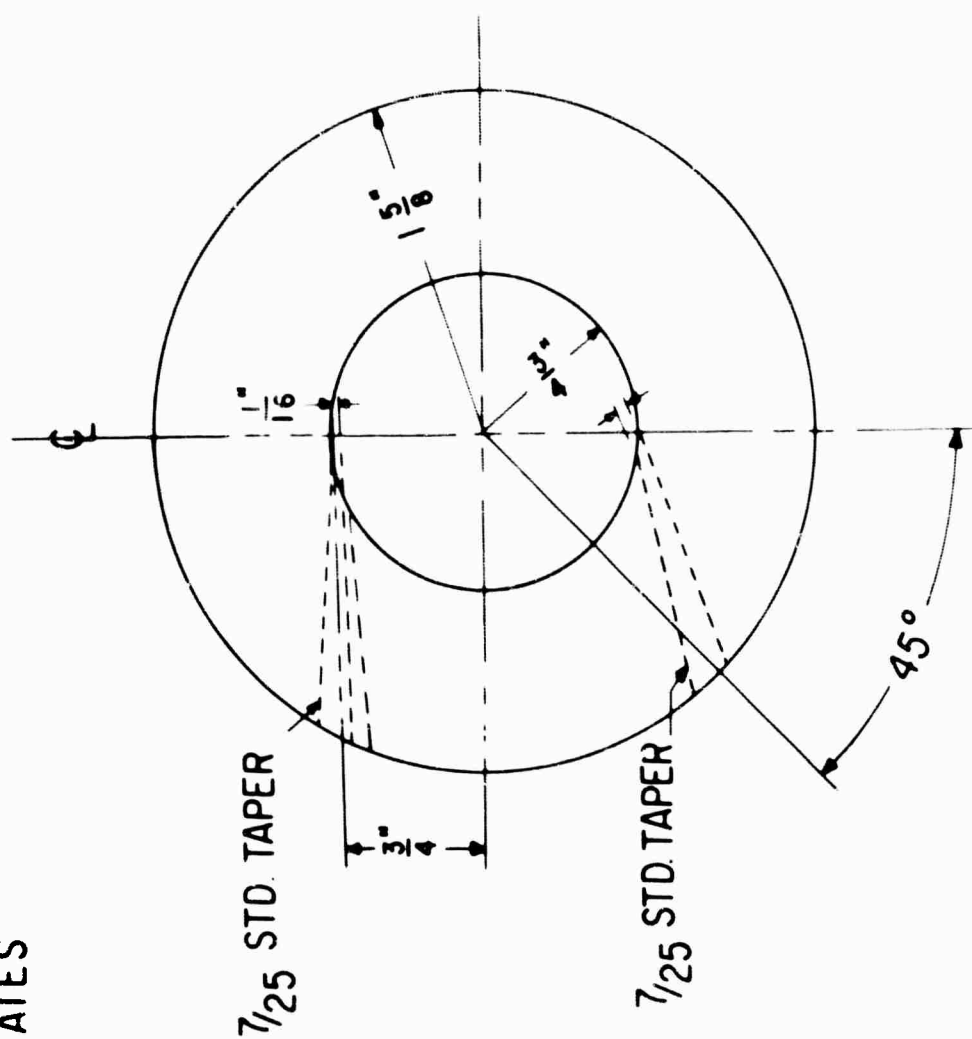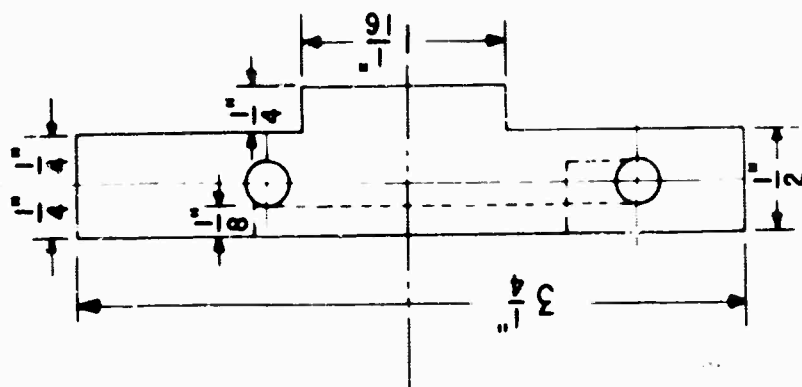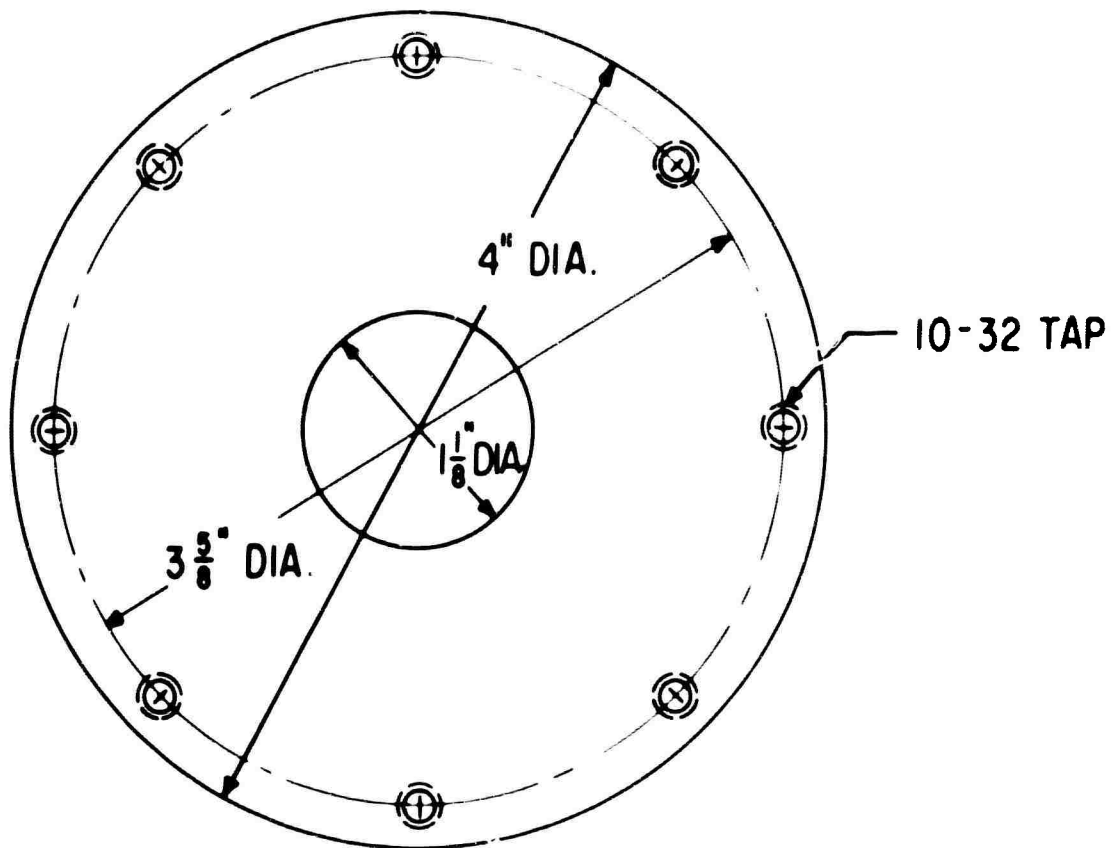
$\frac{1}{4}$" THICK
#316 STAINLESS STEEL

Figure 5

-13-

TEFLON BEAKER

250 cc

BEVELLED FILLER

RING TO TIGHTEN DOWN
BEVELLED FILLER

$\frac{1}{8}$"

$\frac{1}{4}$"

$\frac{1}{8}$"

$\frac{1}{2}$"

$\frac{3}{4}$"

RESERVOIR

ADAPTER

$\frac{1}{2}$"

$\frac{1}{8}$"

$\frac{1}{8}$"

$-\frac{1}{8}$"

$\frac{1}{4}$"

$\frac{1}{8}$"

$\frac{1}{2}$"

1"

$\frac{3}{4}$"

$\frac{3}{4}$"

KNURL

Figure 6

-14-

0.040" DIA.

0.125" DIA.

$\frac{1}{32}$"

$\frac{1}{8}$"

7/25 STD. TAPER

7/25

$\frac{3}{8}$"

1"

.040"

$\frac{1}{2}$"

Ⓐ

.020"

$1\frac{1}{2}$"

INLET 8 OUTLET PLUGS

INLET PLUG: Ⓐ = 0.040"
OUTLET PLUG: Ⓐ = 0.085"

1" SQUARE

$\frac{1}{2}$"

$\frac{1}{8}$"

$\frac{1}{4}$"

$\frac{3}{4}$"

STOPCOCK

3° TAPER

1"

$\frac{1}{4}$"

1"

$\frac{3}{4}$"

7/25 STD.
TAPER PLUG
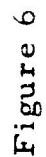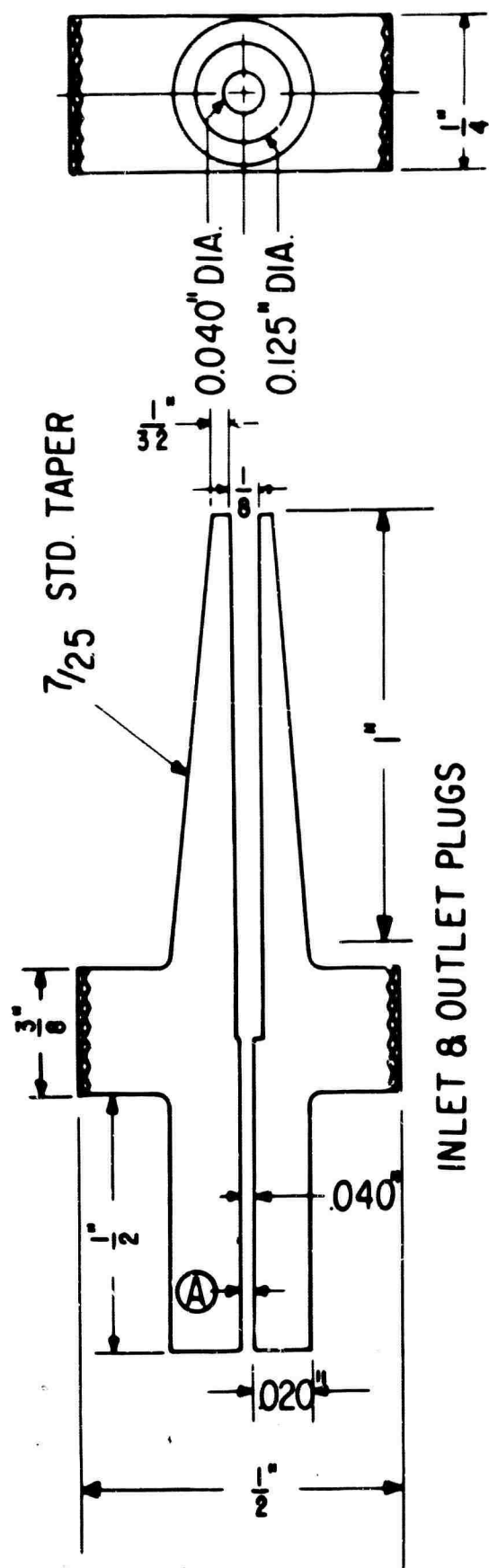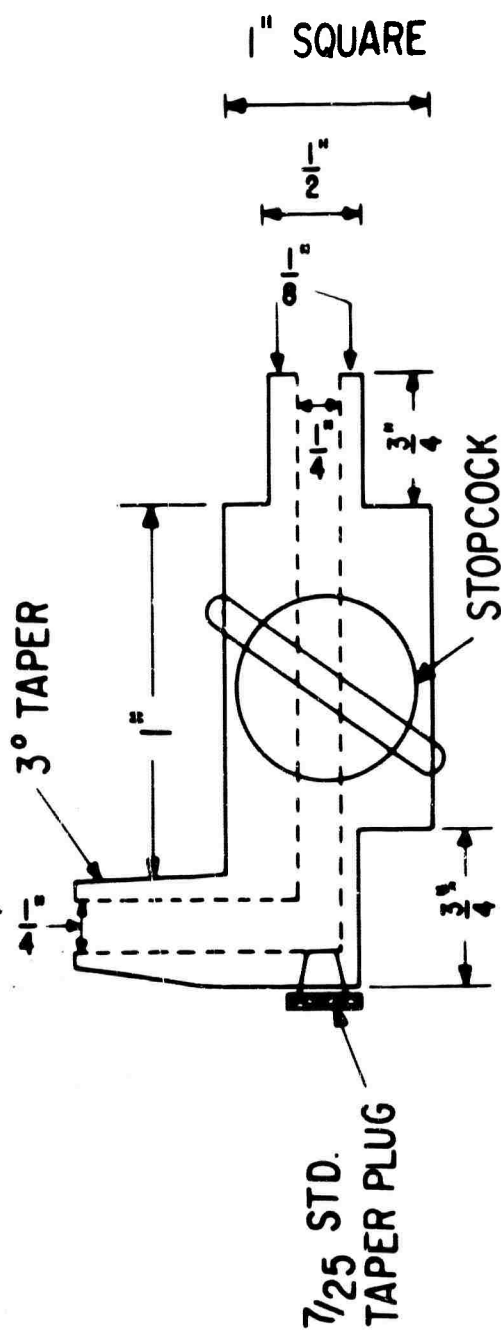
SAMPLING ELBOW

Figure 7

-15-
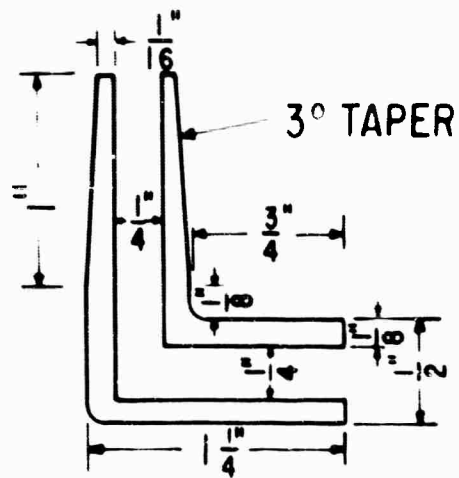
CONNECTOR ELBOW

CONNECTOR PLUG

CELL CONNECTOR

Figure 8

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III. EQUIPMENT DESIGN AND CONSTRUCTION (Cont'd)

a. Cell Design (Cont'd)

When the upper stopcock (C) is closed, the 2 cells A and B are separated. Closing the lower stopcock (D), and removing the drain plug in part D allows the electrolyte from the working cell to be drained.

The use of 1/2" O. D. Teflon tubing combined with the stacked configuration of the 2 cells provides bubble free operation. By stacking the two cells, and employing tubing of large diameter, the bubbles formed will rise through the cell exits and therefore cannot collect in either cell. The upper electrolyte reservoir, (not shown), is mounted above the air thermostat and is a heated Teflon beaker. This arrangement permits simple addition or removal of electrolyte or water.

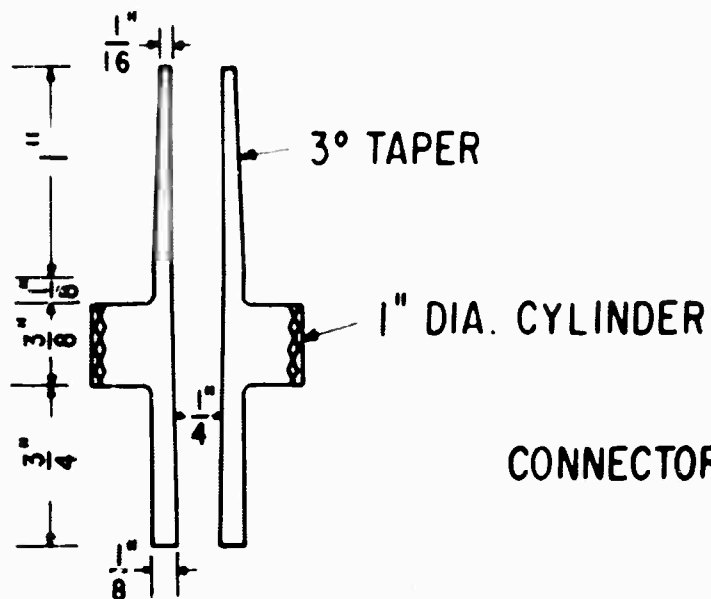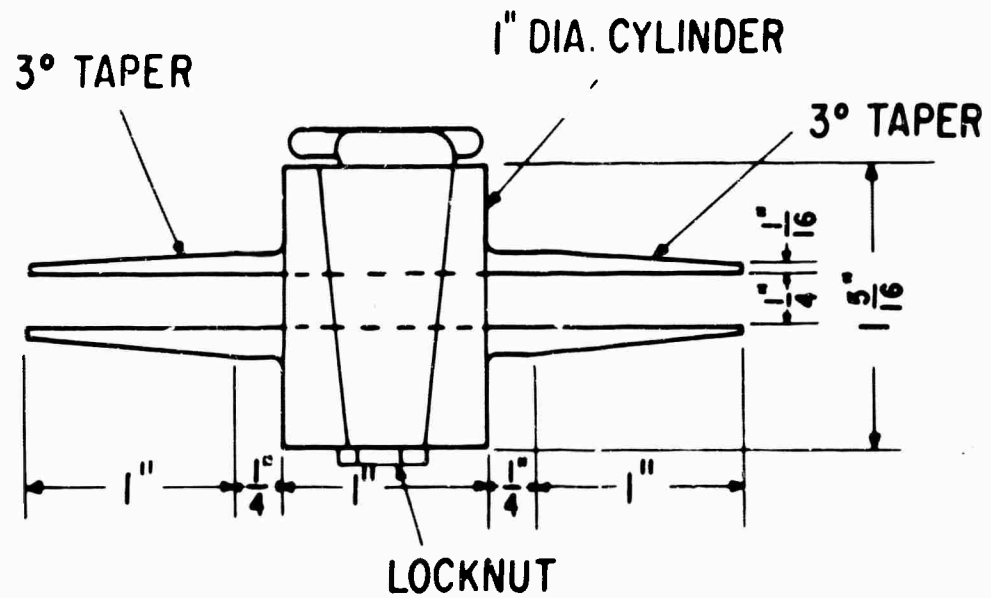The electrolyte flows from the upper reservoir through the cells and into the lower reservoir (E) by gravity. The electrolyte is pumped from the lower reservoir by a Teflon bellows pump to the upper reservoir. Thus, circulation can be controlled by two methods; first by the valve immediately above the lower reservoir E, (See Figure 1) and second, by the rate of pumping. If operation with non-flowing electrolyte is desired, as when collecting material balance data, the pump may be turned off and the electrolyte will seek a level, filling both cells completely.

III.   EQUIPMENT DESIGN AND CONSTRUCTION (Cont'd)

a.   Cell Design (Cont'd)

In the stacked cell design a new method of mounting was employed, allowing precise and rapid alignment of the two cells. This assured leak-tight operation.

The traps, (F), are included for collection of electrolyte seepage through the electrodes.

b.   Electrical Measuring Equipment

The use and operating principle of the Kordesch-Marko interrupter have been previously described (1, 2). An improved version of the original circuit incorporating a self-contained current control, and measuring bridges with more precise balance adjustment has been built and tested. The new circuit diagram is shown in Figure 9. These features allow continuous variation of the cell current from 20 micro-amps up to 12 amps without the use of an external resistance adjustment. The modified bridge circuit permits potential measure- ments to be made even when the anode and cathode voltages are reversed (a feature lacking in previous models). While the bridge voltages do not include IR losses, these are readily obtained by direct measurement across the cell terminals with a potentiometer. A strip chart recorder and a time-averaging circuit are used to monitor the average cell voltage.

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UNLESS OTHERWISE SPECIFIED USE THE FOLLOWING —

APPLIED PRACTICES	SURFACES	TOLERANCE ON MACHINE DIMENSIONS
		FRACTIONS	DECIMALS	AN
	✓	+ −	+ −	+ −

POWER ON OFF

S_1

3A

PL

(2) POWER STATS

T_1 9T51Y6171

1N2129 (5 IN SERIES)

CELL ON OFF

S_2

CURRENT

CURRENT ADJ
COARSE   FINE

T_2 F90X

115V

20V

20V

250 Ω 5 w

250 Ω 5 w

1N1696

1N1696

33 1/2w

100 10T HELIPOT

S_5

BALANCE

REVERSE

200 μf/20v

V_1

T_3 F90X

115v

2

20v

250 Ω 5 w

250 Ω 5 w

1N1696

1N1696

33 1/2w

100 10T HELIPOT

S_6

BALANCE

REVERSE

200 μf/20v

V_2

A

Figure 9

c.   Gas Flow Meters and Associated Equipment

Control of liquid fuel flow rates to the cell is achieved by the use of a constant speed syringe drive (See Appendix C for calibration). The gaseous fuels present a more difficult problem of control and measurement. Since the required flow rates cover a wide range, (0.1 cc/min. up to 3 cc/sec) a capillary flow meter was considered most suitable.

In any system that employs low flow rates the problem of minimizing the system volume becomes difficult. This factor seriously affects the system's response to a flow rate change. The use of Teflon "spaghetti" tubing (size 0.075" I.D.) was found satisfactory. The cell chambers were reduced to a minimum volume, and the H_2O bubblers (to control the H_2O content of the fuel gas) were designed for low volume operation. The condensers and traps on the fuel cell exits were designed to provide low volume, large capacity operation.

The flow meters were designed by the application of Poiseuille's equation (See Appendix B for sample calculation). The useful flow-rate range of a given capillary was extended by use of a dual manometer using Hg as one fluid and water as the other. See Figure 10 for details. Incorporated into this design were provisions for simple, rapid purging. When operating at low flow rates (0.1 cc/min to 1/2 cc/min), the H_2O manometer proves adequate.

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FLOW METER

CAPILLARY

$^{7}/_{25}$ ₷

$^{14}/_{35}$ ₷

TOPCOCK

$^{12}/_{5}$ SOCKET JOINT

STOPCOCK

3 WAY STOPCOCK

$^{12}/_{5}$ SOCKET JOINT

VENT

STOP COCK

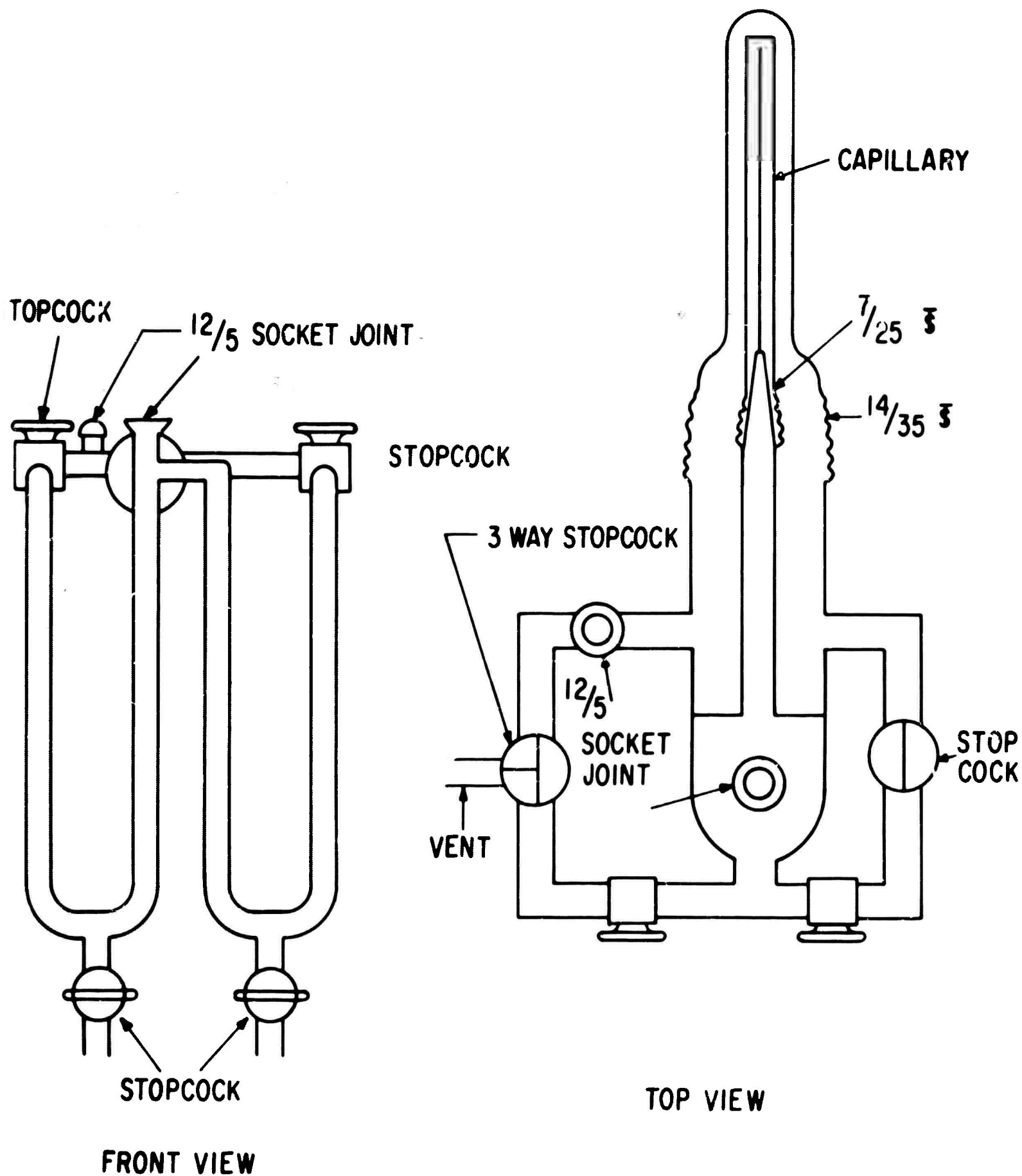STOPCOCK

FRONT VIEW

TOP VIEW

Figure 10

III. EQUIPMENT DESIGN AND CONSTRUCTION (Cont'd)

c. Gas Flow Meters and Associated Equipment (Cont'd)

For the higher flow rates, larger pressure differentials are needed.
The Hg leg is used to indicate these flow rates. To prevent blowout
of the H_2O manometer, a stopcock was included to allow closure of
the H_2O leg. Use of a bypass system permits the flow of gas at a
rate higher than normal, for purging the lines and calls rapidly.
Inside the oven (See Figure 1) a gas flow connector block is employed,
which in combination with a second capillary flow meter, allows quick
changeover from one fuel to another without delay for excessive
purging. The changeover is accomplished by switching two plugs
in the block.

The gas flow control panel (See Figure 11, C) permits precise,
accurate measurements of fuel, O_2 or air flow rates, necessary for
the planned material balance experiments.

Associated with the panel are the "fine control valves" (NUPRO
Inc., Cat. No. B4MD) and line filters (Cat. No. B4F, Nupro) which
prevent dust particles from plugging the capillaries or valves.

The gases can be passed through the low gas volume water bubblers
which are housed in a separately thermostated box (Figure 11, D) so
that the H_2O content of the gases may be controlled by varying the
temperature of the bubbler (See Reference 3 for required carbon de-
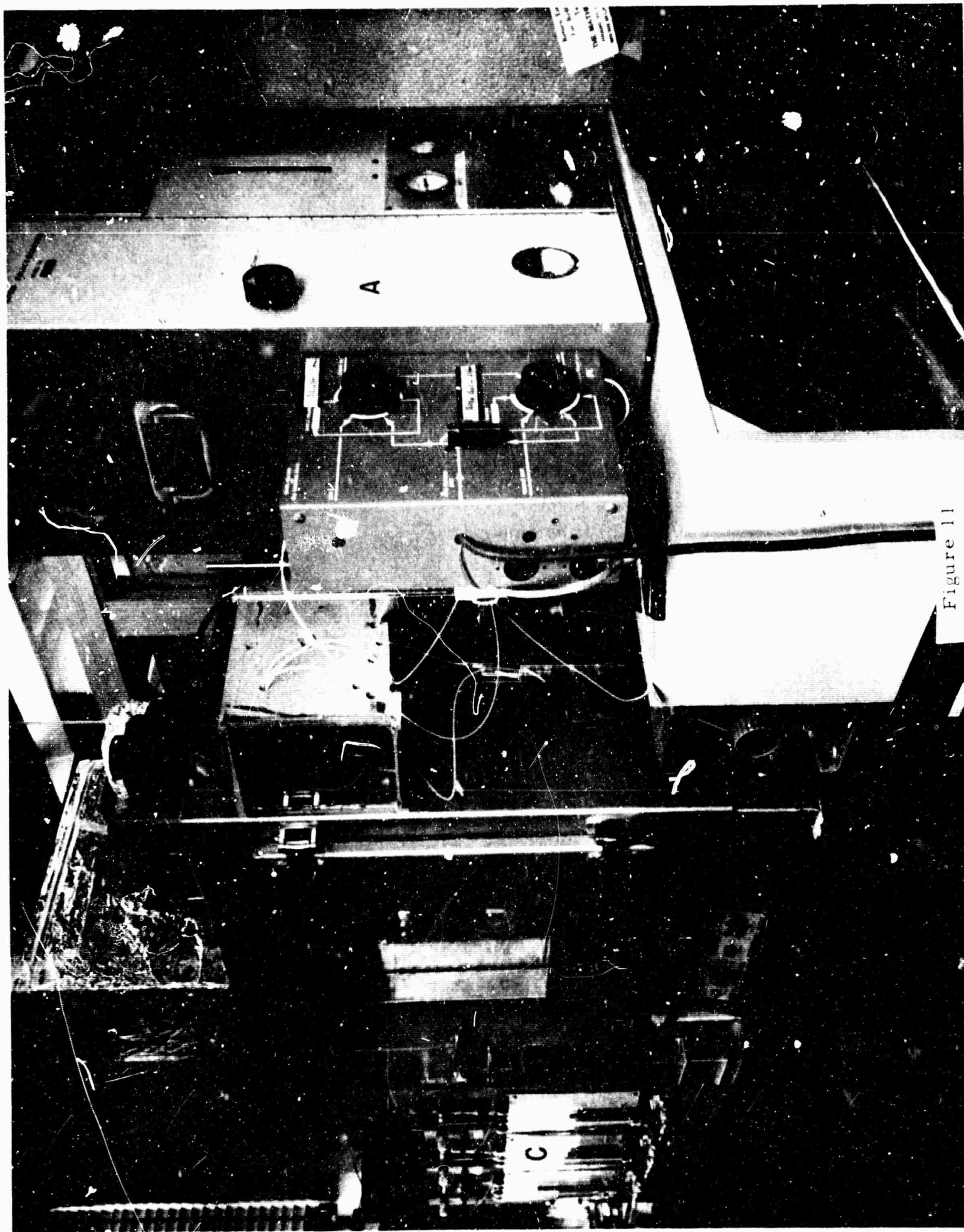position data - also see Page 28 this report.

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Figure 11

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III. EQUIPMENT DESIGN AND CONSTRUCTION (Cont'd)

d. Liquid Fuel Feed System

Accurate control of liquid fuel flow rates is accomplished by the use of a variable speed, precision ($\pm$ 0.01%) syringe drive (Harvard Apparatus Co., Model 600-2-200). This device performed very well during the CH_3OH-Dow Electrolyte life test, and in previous material balance experiments.

Because of the low flow rates required for liquid hydrocarbons, calibrations on small-volume syringes (10-30CC) was performed (See Appendix C).

In conjunction with the liquid fuel feed, it was necessary to provide an interface control device. This prevents pressure fluctuations due to uneven vaporization of the fuel entering the air thermostat. This equipment provides a sharp thermal gradient by employing a cooled zone immediately followed by a heated zone.

When operation on gaseous fuels indicates a need for H_2O addition either to the fuel or to the electrolyte, the syringe drive can be employed to maintain a constant H_2O feed rate.

e. Gas Analysis Equipment

A chromatographic unit (Figure 11, A) along with an exit gas flow measuring device was integrated into the fuel cell system.

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III.   EQUIPMENT DESIGN AND CONSTRUCTION (Cont'd)

e.   Gas Analysis Equipment (Cont'd)

A condenser apparatus was used to remove H_2O and other high boiling constituents from the sample to be analyzed (See Figure 12). The remaining gas was then passed through two sampling valves in series (indicated by S in Figure 12). A modified Perkin-Elmer Vapor Phase Chromatograph (Model 154D) allows the sample to be passed through either of two columns. The sampling valves and dual-column chromatograph allow complete analysis of the reaction product gas, while minimizing sample size. One column is (Molecular Sieve 5A) employed to determine the low molecular weight hydrocarbons and permanent gases, while the other (silica gel) is used for the high molecular weight hydrocarbons and CO_2. The exit gas flow rate was measured with a mercury-seal piston flow meter (Porter Flow-meter Calibrate Model 1052) in parallel with the chromatograph.

IV.   EXPERIMENTS AND RESULTS

a.   Evaluation and Testing of Dow Cs_2CO_3

The performance of any fuel cell can be affected by impurities in the electrolyte. Since the lot of Cs_2CO_3 obtained from Dow analyzed out of specifications (complete analysis in Appendix A), a fuel cell life test was performed using CH_3OH fuel taking advantage of our previous experience.
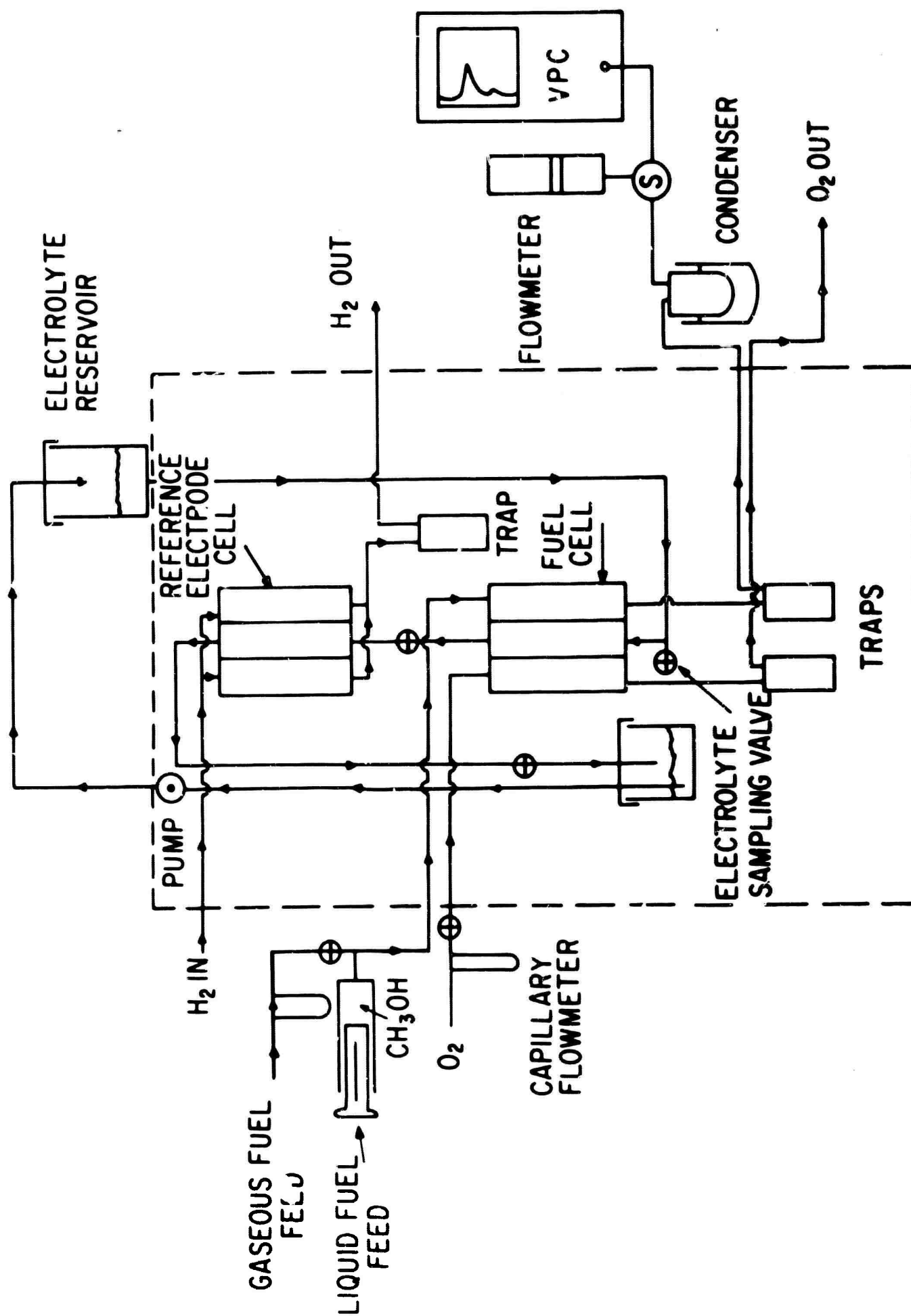
Figure 12

a.   Evaluation and Testing of Dow Cs_2CO_3 (Cont'd)

The performance on CH_3OH obtained previous to this contract work is known and reproducible; these factors were considered an .m-portant basis for the electrolyte evaluation.

The fuel cell contained Pt electrodes constructed for a maximum of reliability.   The electrolyte concentration was adjusted to a $135^{\circ}C$ boiling point and the fuel was a 52 wt. % CH_3OH solution fed at a rate of 0.009 cc/min.

All of the important variables for this system have been studied previously, so that the results of running such a cell could be related to the electrolyte acceptability for fuel cell use.   This is a necessity if further meaningful study of the hydrocarbon fuel cell is to be performed with this electrolyte.

Electrolyte analyses were performed on samples taken before, during, and after the CH_3OH fuel cell life test in order to determine any change in impurity level in the electrolyte which may have taken place during cell operation.

Addition of catalysts to the electrolyte and the effect of H_2O partial pressure on the O_2 cathode performance were also investigated.

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IV. EXPERIMENTS AND RESULTS (Cont'd)

b. Life Test Procedure

Since a long run on an organic fuel was planned, it was necessary to establish the appropriate conditions for avoiding carbon deposition from the fuel. The methods for establishing the conditions of carbon-free operation at equilibrium with any CH or CHO fuel or fuel mixture have been discussed previously(3). Briefly, the carbon deposition boundary for the desired operating temperature ($130^{\circ}C$) is located (See Figure 30, Reference 3), and the atom fractions of C, H, and O are noted. Then,

$$
\text{let} \qquad \left.\begin{array}{l} CH_3OH = 1 \text{ mole} \\ H_2O = \quad X \text{ moles} \end{array}\right\} \text{ Fuel mixture}
$$

$$
f_c = \frac{C}{C + H + O} = \frac{1}{1+(4+2X) + (1+X)}
$$

$$
\therefore \quad f_c = 0.091 \text{ (From Figure 30, Reference 3)}
$$

$$
= \frac{1}{1+4+2X+1+X}
$$

$$
\therefore \quad x = 1.63 \text{ moles } H_2O \text{ per mole } CH_3OH, \text{ or } 32 \text{ g}CH_3OH + 29.5\text{g}H_2O
$$

$$
\frac{32\text{g}CH_3OH}{61.5\text{g Solution}} \times 100 = 52\% \ CH_3OH
$$

Therefore, a fuel mixture containing 52 weight percent methanol (or less) is necessary in order to insure that no carbon deposition will occur at $130^{\circ}C$, at equilibrium.

IV. EXPERIMENTS AND RESULTS (Cont'd)

b. Life Test Procedure (Cont'd)

The cell was operated at $130^{\circ}C$ on 52 wt. % CH_3OH for 24 hours a day for 563 hours.

The daily testing of the cell began at 0 hours and proceeded every day with a reading of the anode versus cathode, anode versus H_2 reference, and cathode versus H_2 reference voltage under load. A current density-voltage curve was taken at least once a day, in order to check for performance changes, while the overall cell voltage was recorded continuously during the life test.

The current density-voltage curves are a direct index of cell performance, and can be used to judge the effect of the electrolyte on cell performance during extended operation. The cell performance data were determined by the use of the previously described Kordesch-Marko interrupter and do not include I. R. losses.

Table I is a log sheet of the life test, and notes all operations of any consequence which were performed on the cell.

TABLE I
Life Test Log
Cell #66 4/8/63/G. J. H.
$CH_3OH(g)$ (Pt)/Cs_2CO_3/O_2 (Pt)
T = 130°C

Date	Time	Hours	E-i Curve	H₂O Add.	Comments
4/8/63	10 PM	0	X		Start up
4/9/63	8 AM	10	X	5CC	Starting H_2O
	10 AM	12		5CC	buildup in
	11 AM	13		20CC	electrolyte due
	1 PM	15		10CC	to addition rate
	2 PM	16		15CC	during night
	3 PM	17		15CC	
	4 PM	18			
4/10/63	8 AM	34	X		
	10:30 AM	36.5		10CC	
	11:15 AM	37.25		15CC	
4/11/63	8 AM	58	X		
	10 AM	60		20CC	
	11 AM	61		10CC	
	12 PM	62		10CC	
	1 PM	63		10 CC	
	2 PM	64		10 CC	
	3 PM	65		10 CC	
	4 PM	66		10 CC	
4/12/63	8 AM	82	X		Compared E-i
	9 AM	83		10CC	curve @82 to 84
	10 AM	84	X		hrs and noted
	11 AM	85		10CC	improvement
	12 PM	86		10CC	
	1 PM	87		10CC	
	2 PM	88		10CC	
	3 PM	89			Added more electrolyte
4/13/63	1 PM	113			AC; CR; AR
4/14/63	2 PM	p38			AC; CR; AR

TABLE I (Cont'd)
Life Test Log
Cell #66 4/8/63/G. J. H.
$CH_3OH(g)$ (Pt)/Cs_2CO_3/O_2 (Pt)
T = 130°C

Date	Time	Hours	E-i Curve	H₂O Add.	Comments
4/15/63	2 PM	162	X	20CC	Pump repaired
	3 PM	163		10CC	
	4 PM	164		10CC	
	5 PM	165		10CC	
4/16/63	8 AM	180	X		
	10 AM	182		10CC	
	11 AM	183		10CC	
	1 PM	185		10CC	
	2 PM	186		10CC	
	3 PM	187		10CC	
4/17/63	8 AM	204	X		Electrolyte Sample
	9 AM	205		10CC	Taken
	11 AM	207		10CC	
	1 PM	209		10CC	
	2 PM	210		10CC	H₂O bubbler on O₂ line
4/18/63	8 AM	228	X		
	10 AM	230			Boiled CH_3OH to remove
	11 AM	231	X (Better)		air
	12 PM	232		10CC	
	1 PM	233		10CC	
	2 PM	234		10CC	
	3 PM	235		10CC	
	4 PM	236		10CC	
4/19/63	8 AM	252	X		
	10 AM	254		10CC	
	11 AM	255		10CC	
	1 PM	257		10CC	
	2 PM	258		10CC	
	3 PM	259		10CC	
4/20/63	5 PM	285			AC; CR; AR
4/21/63	No Entry				

TABLE I (Cont'd)

Life Test Log
Cell #66 4/8/63/G. J. H.
$$CH_3OH(g) \ (Pt)/Cs_2CO_3/O_2 \ (Pt)$$
$$T = 130°C$$

Date	Time	Hours	E-i Curve	H_2O Add.	Comments
4/22/63	8 AM	324	X		
	9 AM	325		30CC	
4/23/63	8 AM	348	X		
	10 AM	350		10CC	O_2 bubbler filled
4/24/63	10 AM	374	X		
	10:30 AM	374.5		10CC	Remove O_2 bubbler
	12:30 PM	377.0	X		Better performance
4/25/63	9 AM	397	X		
	10 AM	398		10CC	
	1 PM	401		10CC	
	4 PM	404	X		
4/26/63	8 AM	420	X		
	10 AM	422		10CC	
	11 AM	423		10CC	
4/27/63	1 PM	449		20CC	AC; CR; AR
	4 PM	452		10CC	AC; CR; AR
4/28/63	4 PM	475			AC; CR; AR
4/29/63	8 AM	490	X	10CC	
	9 AM	491		10CC	
	10 AM	492		10CC	
	11 AM	493		10CC	
	1 PM	495		20CC	
	4 PM	498		10CC	
4/30/63	8 AM	514	X		
	9 AM	515	add 1cc H_3BO_3 Solution		$\left(\dfrac{1gr \ H_3BO_3}{100cc \ soln}\right)$
	10 AM	516	add 1cc H_3BO_3 Solution 9CC H_2O		
	11 AM	517	add 1cc H_3BO_3 Solution 9CC H_2O		
	1 PM	519	add 1cc H_3BO_3 Solution 9CC H_2O		

TABLE I (Cont'd)
Life Test Log

Cell #66 4/8/63/G. J. H.

$CH_3OH(g)$ (Pt)/Cs_2CO_3/O_2 (Pt)

T = 130°C

Date	Time	Hours	E-i Curve	H_2O Add.	Comments
4/30/63	2 PM	520		add 2cc H_3BO_3 Solution 8CCH_2O	
	3 PM	521		add 2cc H_3BO_3 Solution 8CCH_2O	
	4 PM	522		add 4cc H_3BO_3 Solution 5CCH_2O	
	5 PM	523		add 4cc H_3BO_3 Solution 5CCH_2O	
5/1/63	8 AM	538		add 4cc H_3BO_3 Solution	
	8:30 AM	538.5	X		
	11 AM	541		add 2cc H_3BO_3 Solution 7CCH_2O	
	12 PM	542		11CC H_3BO_3 $\leq H_3BO_3$ = 0.75 eq./100eq. Cs_2CO_3	
	3 PM	545		11CC H_3BO_3 $\leq H_3BO_3$ = 1.0 eq./100eq. Cs_2CO_3	
	5 PM	547		10CCH_2O	
5/2/63	8 AM	562		20CCH_2O	
	8:30 AM	562.5	X		
	9:AM	563			Cell used for other experiments

c.   Life Test Results

The life test results are summarized in Figure 13, with marked points (A through G) indicating the times for which the current density-voltage curves are shown in Figures 14 through 20.

The following observations summarize the more important aspects of the life test results:

1.   The electrolyte, which was flowing (Ca 2cc/min) throughout the test, remained crystal clear, even after 563 hours of operation. This visual test is quite sensitive to a slight amount of colored impurities, such as transition metals and organic matter.

2.   In order to maintain high cell performance, periodic addition of water to the electrolyte was practiced (10CC every 4 hours). The procedure found most suitable was that of building up the H_2O content of the electrolyte during the day, while allowing gradual loss over night. It has been previously noted that the partial pressure of H_2O at the anode is a factor in cell performance; operation at a point $5-10^{\circ}C$ below the electrolyte boiling point is optimum.
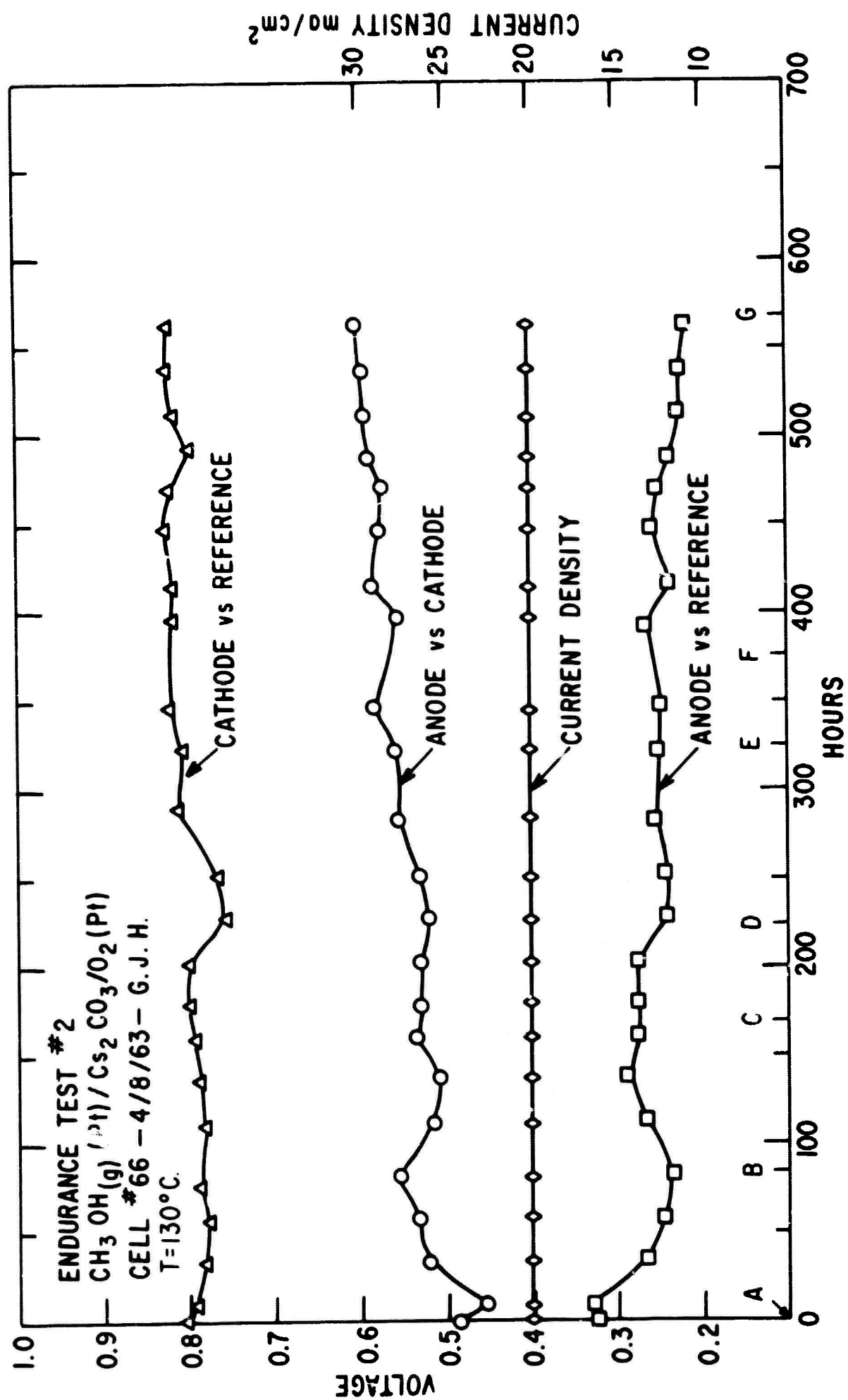
-34-

Figure 13

ENDURANCE TEST #2
$CH_3OH_{(g)}$ (Pt) / Cs_2CO_3/O_2(Pt)
CELL #66 — 4/8/63 — G.J.H.
T=130°C.

CATHODE vs REFERENCE

ANODE vs CATHODE

CURRENT DENSITY

ANODE vs REFERENCE

VOLTAGE

CURRENT DENSITY ma/cm²

HOURS

-35-

AT O HRS.
CELL #66 — 4/8/63 — G.J.H.
$CH_3OH_{(g)}$ (Pt)/Cs_2CO_3/O_2 (Pt)
T=130°C.

CATHODE VS. REFERENCE

ANODE VS. CATHODE

ANODE VS. REFERENCE

VOLTS

ma/cm^2

Figure 14

-36-
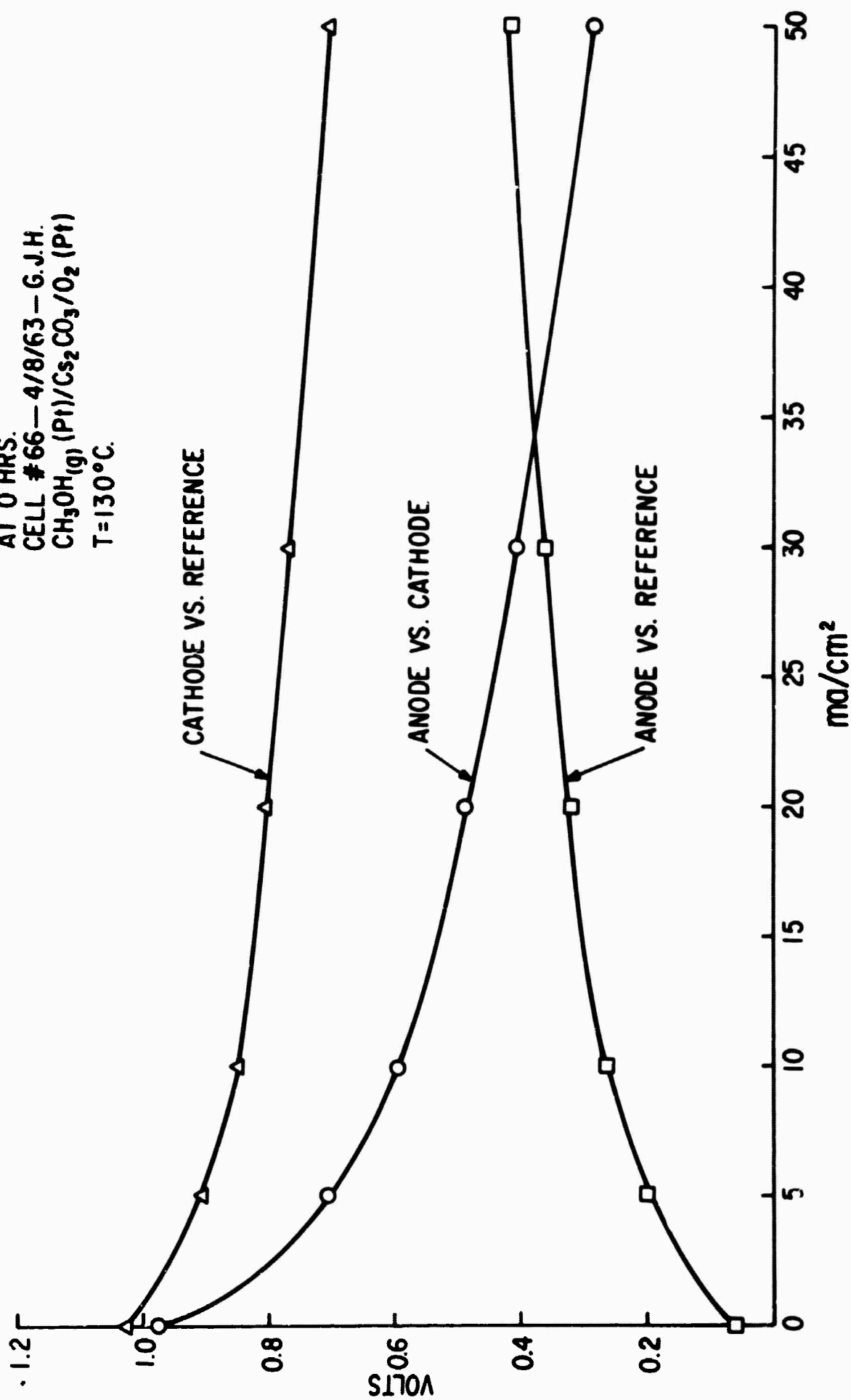
AT 82 HRS.
CELL #66 — 4/8/63 G.J.H.
$CH_3OH_{(g)}$ (Pt)/Cs_2CO_3/O_2(Pt)

T=130°C.
THIS DATA TAKEN BEFORE
ADDITION OF MORE ELECTROLYTE

CATHODE VS. REFERENCE

ANODE VS. CATHODE

ANODE VS. REFERENCE

ma/cm^2

Figure 15

VOLTS

-37-
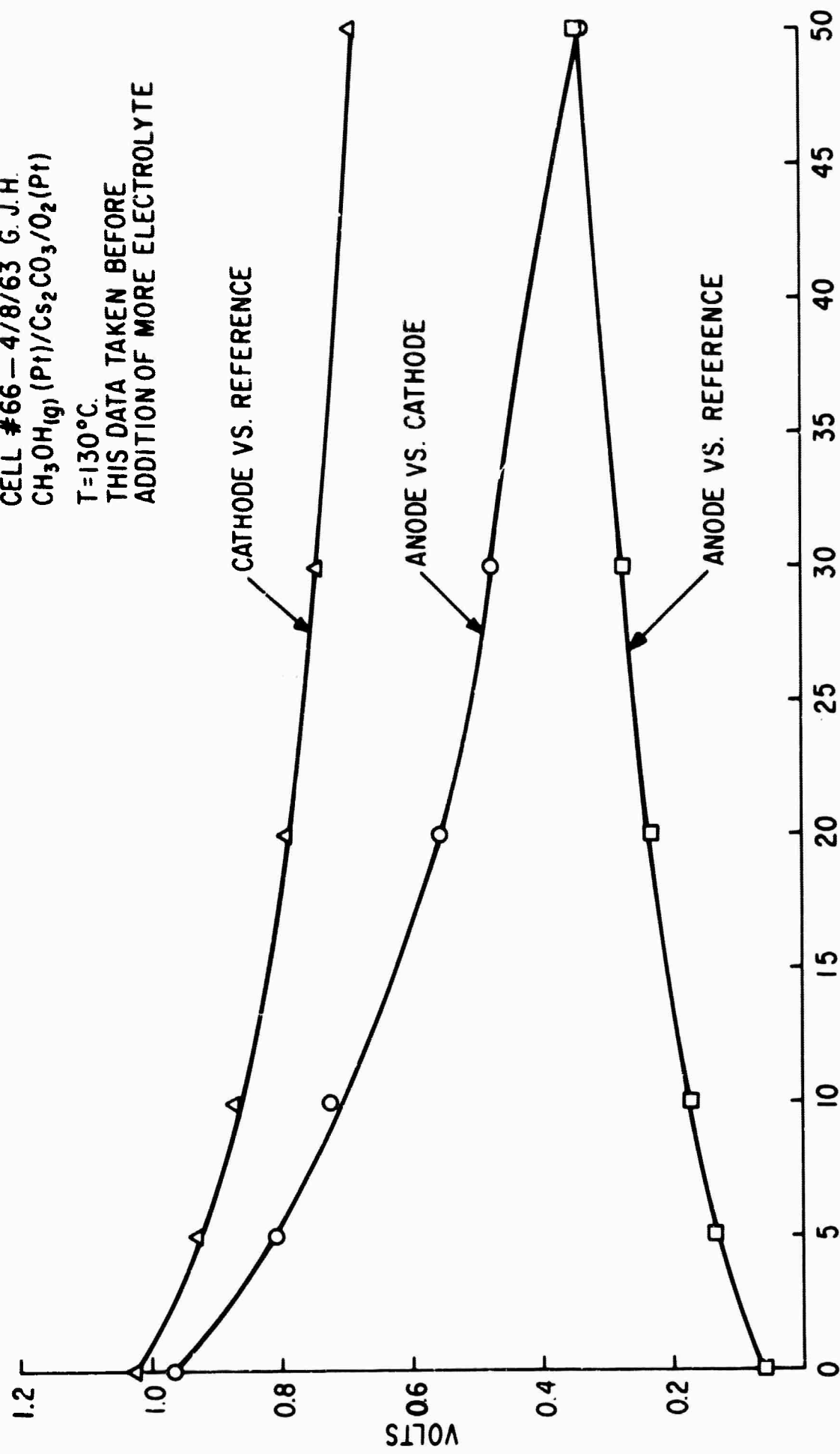
Figure 16

AT 162 HRS.
CELL #66—4/8/63—G. J. H.
$CH_3O\cdot\cdot\cdot_g)(Pt)/Cs_2CO_3/O_2$ (Pt)
T=130°C.
FIRST DATA AFTER ADDITION OF
NEW ELECTROLYTE

CATHODE VS. REFERENCE

ANODE VS. CATHODE

ANODE VS. REFERENCE

ma/cm

VOLTS
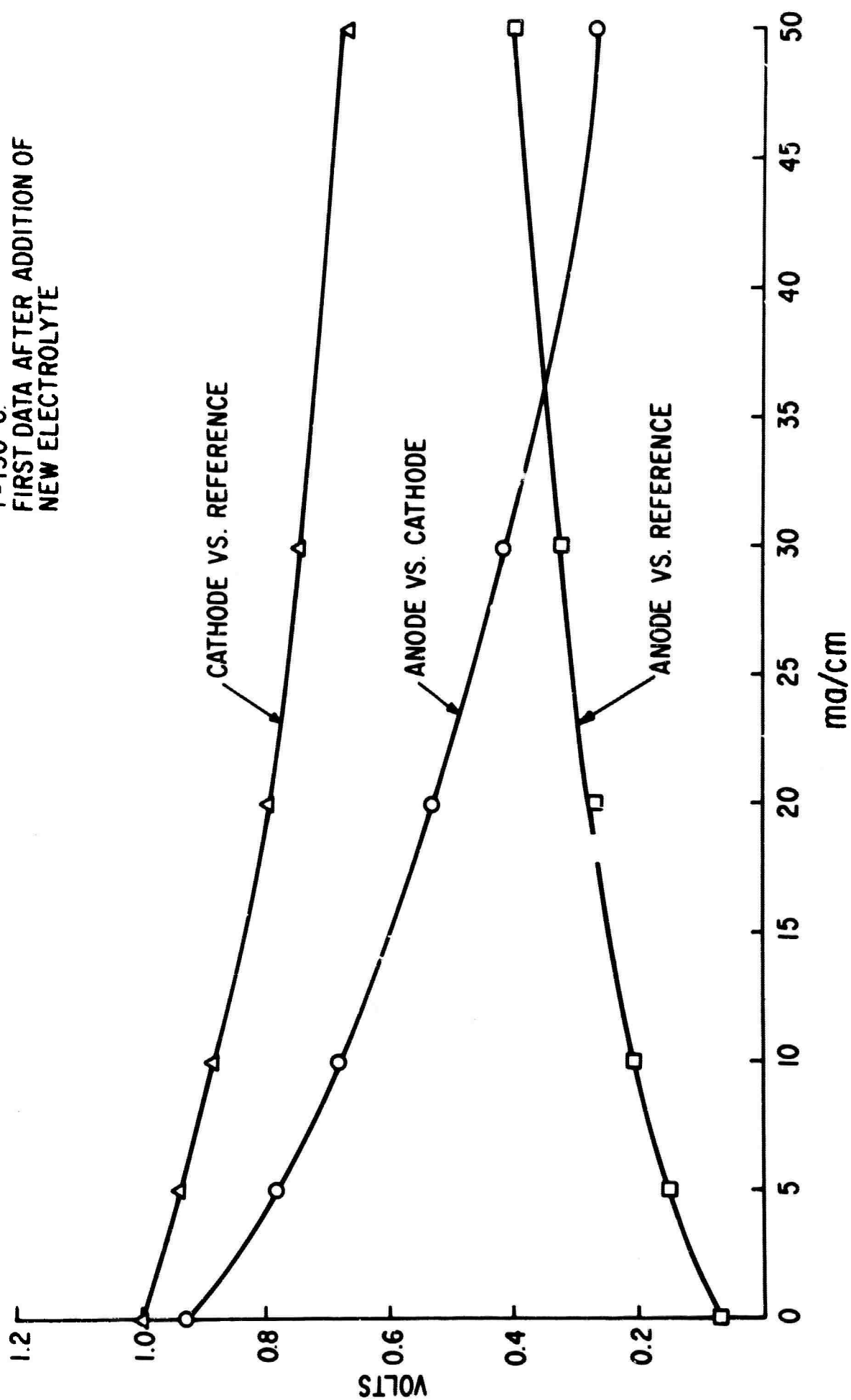
AT 228 HRS.
CELL #66-4/8/63--G.J.H.
$CH_3OH_{(g)}(Pt)/Cs_2CO_3/O_2$ (Pt)

T=130°C.
BEFORE USING BOILED CH_3OH/H_2O FUEL

CATHODE VS. REFERENCE

ANODE VS. CATHODE

ANODE VS. REFERENCE

VOLTS

ma/cm^2

Figure 17

-39-
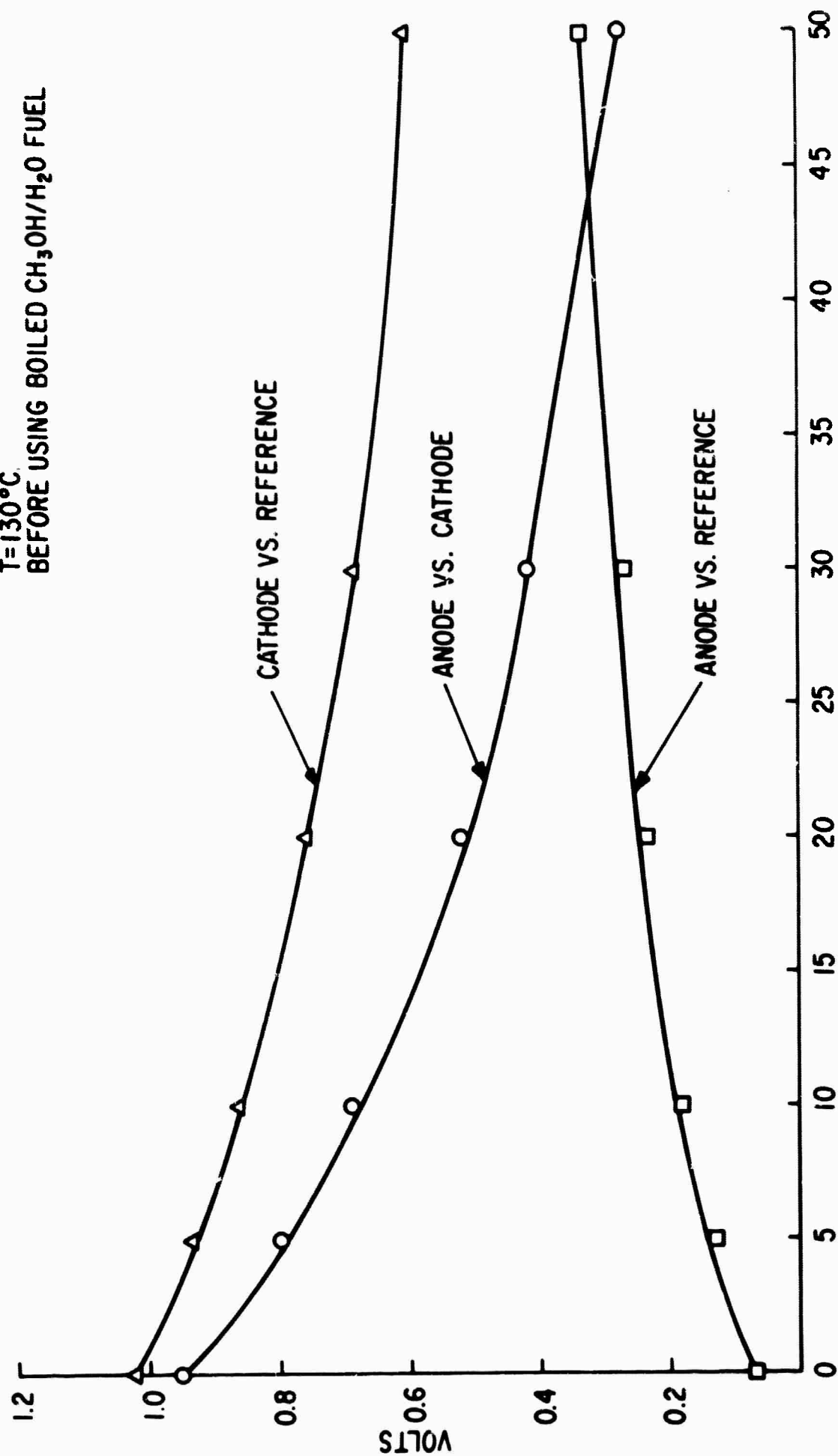
AT 324 HRS.
AFTER USING BOILED CH_3OH/H_2O FUEL
CELL #66 – 4/8/63 – G. J. H.
$CH_3OH_{(g)}$ (Pt)/Cs_2CO_3/O_2 (Pt)
T=130°C.

CATHODE VS. REFERENCE

ANODE VS. CATHODE

ANODE VS. REFERENCE

VOLTS

ma/cm^2

Figure 18

-40-
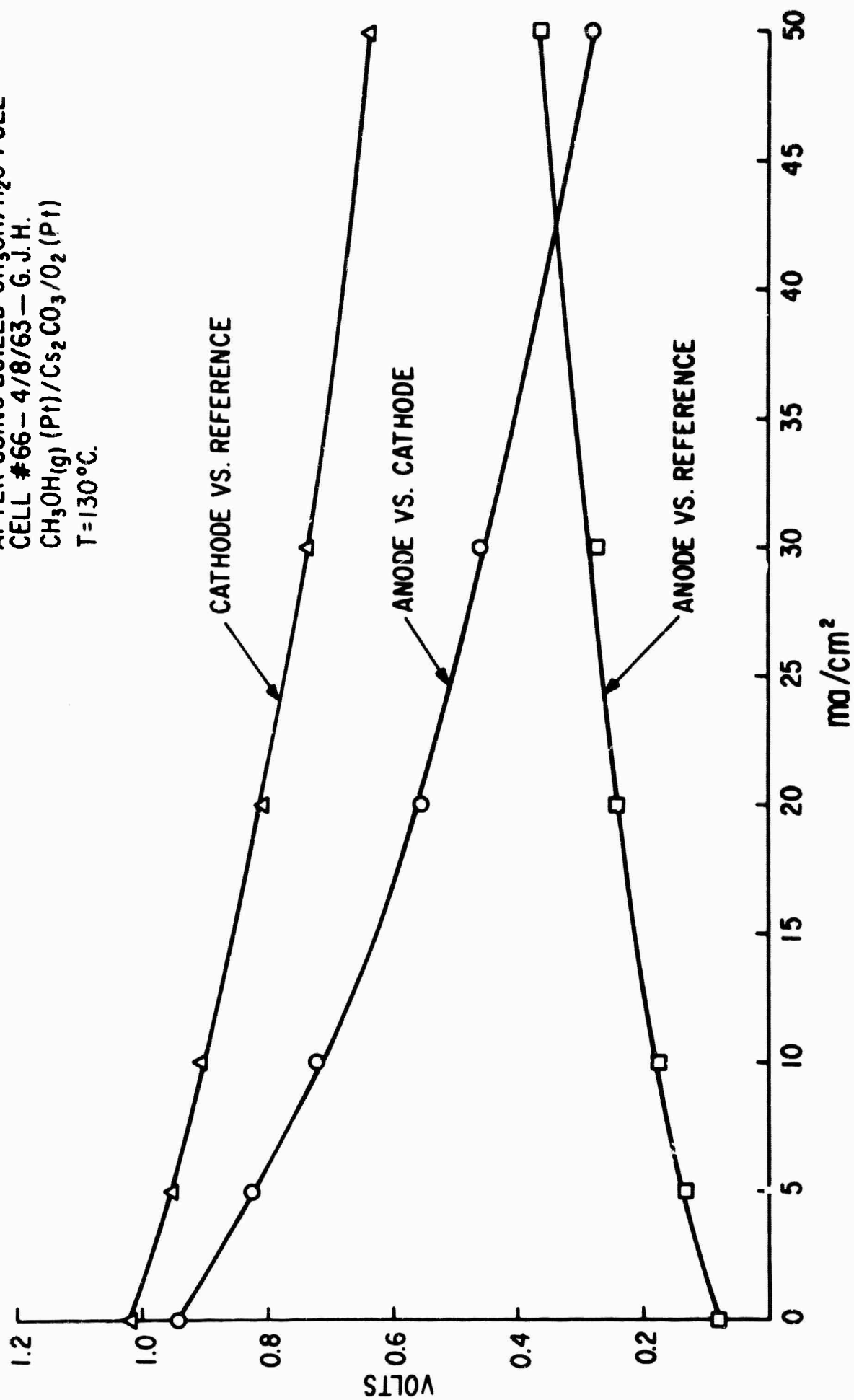
EFFECT OF H₂O BUBBLER IN O₂ LINE
CELL #66 — 4/8/63 — G.J.H.
HOURS = 374
CH₃OH(g)(Pt)/Cs₂CO₃/O₂ (Pt)
T=130°C.

Figure 19

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AT 563 HRS
CELL #66 – 4/8/63 – G. J. H.
$CH_3OH_{(g)}$ (Pt)/Cs_2CO_3/O_2 (Pt)
T=130°C.

CATHODE VS. REFERENCE

ANODE VS. CATHODE

ANODE VS. REFERENCE

VOLTS

ma/cm^2

Figure 20

-42-
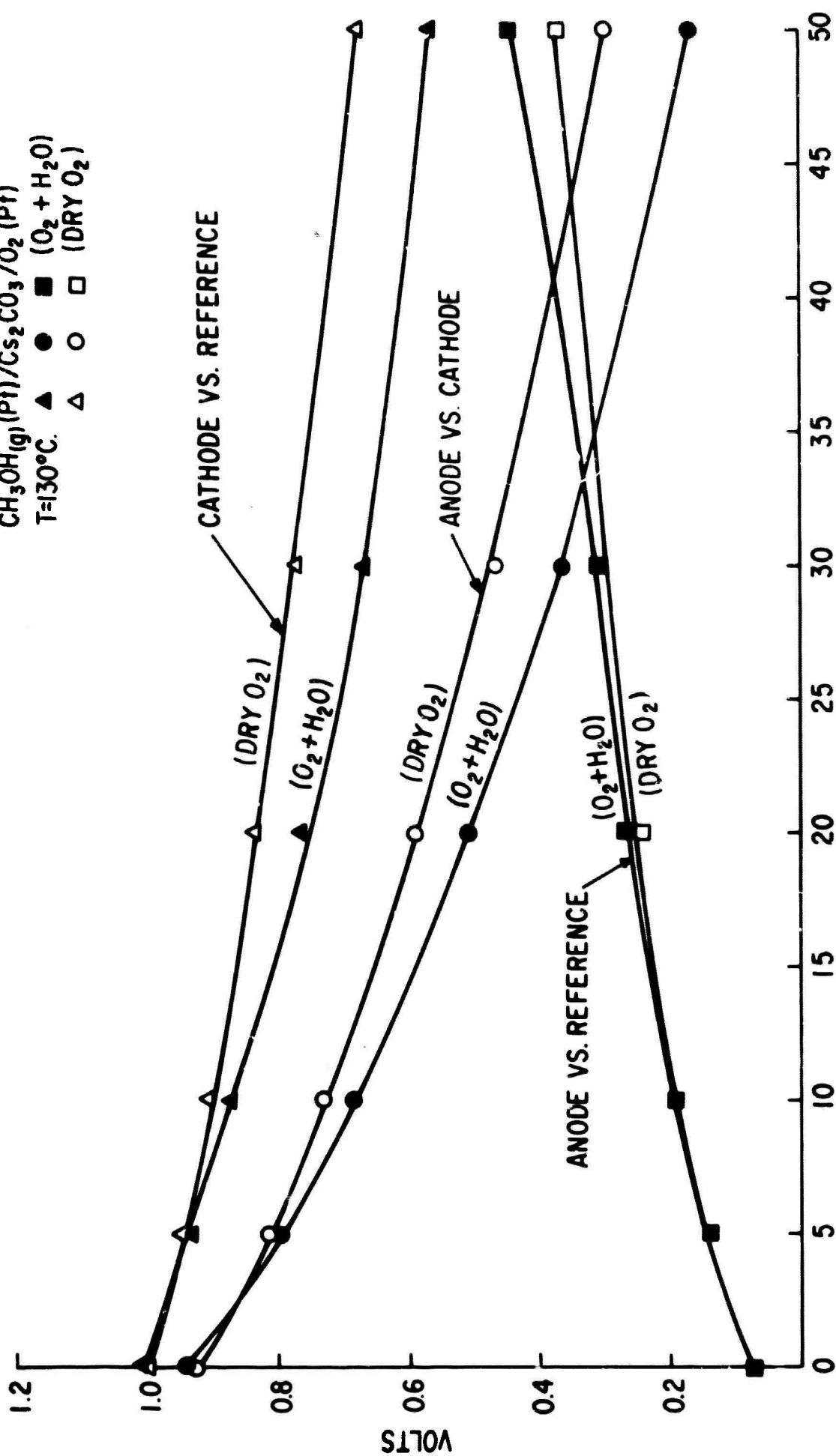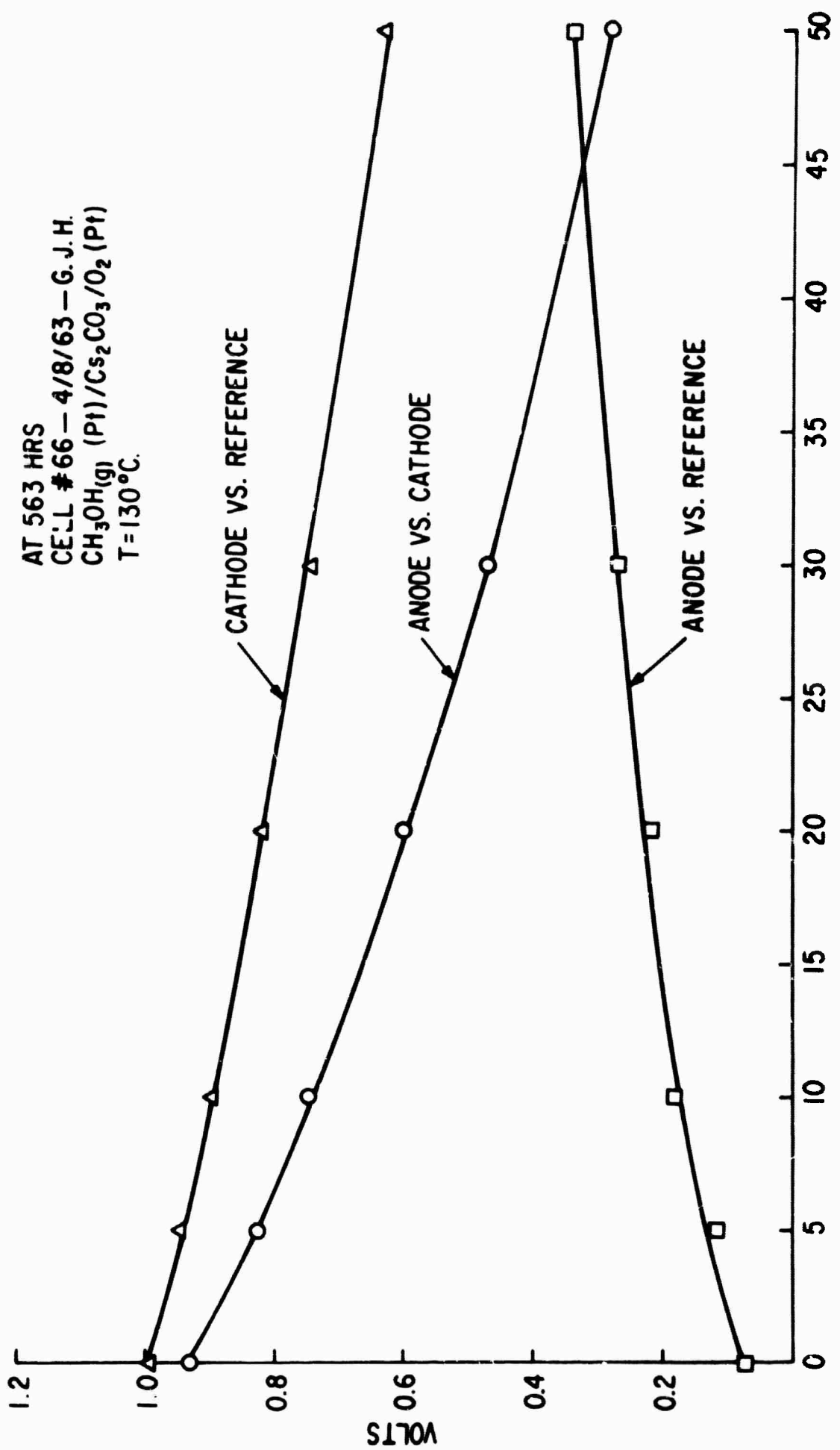
c.   Life Test Results (Cont'd)

3.   Initially the H_2O bubbler in the O_2 line was included in order to limit the rate of water loss from the electrolyte. It was noted, however, that removal of the H_2O bubbler improved the cathode performance (See Figure 19). This effect may be related to a diffusion barrier set up by the $H_2O(\ell)$ in the cathode chamber. Subsequently, the bubbler was removed from the O_2 line.

4.   While the addition of BO_3 to the electrolyte seemed to have no marked effect on performance, a trend toward more steady cell voltages was noted. (See Figure 13).

d.   Electrolyte Analysis Results

1.   The electrolyte samples taken after 200 and 563 hours of operation were submitted, along with a sample of the original electrolyte to chemical analysis. It was important that a clear proof of invariance of the electrolyte be shown by chemical analysis.

The electrolyte was first analyzed for total alkalinity and HCO_3^- content. The results are as follows:

   d.   Electrolyte Analysis Results (Cont'd)

   Sample (1)   200 hours
                Total Alkalinity - 3.74 $\frac{meq.}{gr}$ (Meq/gr of diluted sample)

                HCO_3 - 0.45 $\frac{meq.}{gr}$ (Meq/gr of diluted sample)

   Sample (2)   500 hours
                Total Alkalinity - 3.31 $\frac{meq}{gr}$ (Meq/gr of diluted sample)

                HCO_3 - 0.37 $\frac{meq}{gr}$ (Meq/gr of diluted sample)

The test for the presence of oxidizable organic material in the electrolyte proved negative within experimental error (0.01 meq. per 15CC sample). There is little doubt that after such a long term of operation the electrolyte does not build up any CH_3OH, or incomplete oxidation products; nor is it possible that these products reached the cathode and reacted there since the cathode performance did not decline with time. In addition, no CO_2 was ever found in the cathode compartment. In face, over the long run the performance appeared to be steadily improving. (Figure 13).

The run was terminated at 563 hours because the performance of the cell had successfully demonstrated the fact that the lot of Dow $Cs_2 CO_3$ was adequate for fuel cell performance studies, and further experiments on other fuels were awaiting completion of the life test.

V. CONCLUSIONS

1. The reliability of all new apparatus (cell parts, electrical apparatus, fuel metering and control system, and gas analysis equipment) was proved for extended continuous operating periods.

2. The Dow Cs_2CO_3 was shown to be acceptable for continuous fuel cell operation on organic fuels for periods of at least 563 hours.

3. The invariance of Cs_2CO_3 as an electrolyte for use with organic fuels was proved by life testing and chemical analysis.

4. The reliability and performance of a CH_3OH (Pt)/Cs_2CO_3/O_2 (Pt.) fuel cell indicate that this cell is a promising candidate for engineering development.

VI. PLANS FOR FUTURE WORK

Experiments during the next period will emphasize propane as a model fuel, and will include the following approaches:

1. Steam reforming of the propane just prior to anode reaction, using various catalysts operating at the same temperature as the fuel cell.

2. Preparation and testing of fuel cell anodes containing steam reforming catalysts.

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VI.   PLANS FOR FUTURE WORK   (Cont'd)

3.   Investigation cf non-platinum anode materials for the direct

use of hydrocarbons in intermediate temperature fuel cells

using non-acid electrolytes.

VII. APPENDIX A

Dow Cs_2CO_3 Analyses

	Dow (8/62) 762766		Dow (12/62) 548274		Specs 5/63	
	Dow	GE	Dow	GE	PPM	eq./10^6 eq. Cs
Al	3	3	2	10	3	
Ba	< 7	< 2	< 7	15	< 7	
Ca	4	3	7	30	4	
Fe	5	5	5	5	5	
Sn	< 7	< 3	< 7	< 5	< 7	
B	< 13	< 10	< 13	< 10	< 13	
Cr	< 1	< 1	< 2	< 5	< 1	
Cu	< 1	< 1	< 1	< 2	< 1	
Mg	< 1	< 1	< 1	15	< 1	
Mn	< 1	< 1	< 1	2	< 1	
Ni	< 1	< 2	< 2	< 5	< 1	
Sr	< 1	< 1	< 1	7	< 1	
Ti	< 1	< 2	< 2	< 5	< 1	
Tl	< 1	< 5	< 2	< 10	< 1	
Pb	< 1	< 3	< 2	10	< 1	
Si	13	10	11	5	13	
Li	< 13 (< 302)	< 2	< 13 (< 302)	< 2		
Na	5 (35)	5	59 (418)	48		
K	5 (21)	10	< 20	13 (54)		
Rb	90 (172)	40	< 20	21 (40)		
	(530)					(530) Alkali M
Cl⁻	-	15 (71)	(78)	22 (102)		
F⁻	-	4 (34)	-	5 (42)		(150) Total X⁻
OH⁻	~	~ 0	-	(19,000)	~ 0	-
HCO₃⁻	-	~ 0	-	-	~ 0	-
Cs₂CO₃ (wt)	58%	55.7%	50.6	50.7	~ 50	-

() = eq./10^6 eq. Cs

Above line ⌇⌇⌇ determined from dry sample.

VII.   APPENDIX B

Sample Calculations For Capillary Tube Flowmeters

1.   Select fuel -

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$
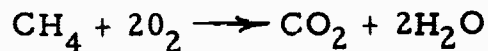
8 e's/mole

2.   Moles Required for 200 ma load

$$\left(0.2 \frac{coul}{sec}\right)\left(\frac{1 \; sec}{1 \; SEC}\right)\left(\frac{1 \; equiv.}{96,500 \; coul}\right)\left(\frac{moles}{8 \; eq.}\right) = 2.59 \times 10^{-7} \text{ moles se.}$$

3.   Convert to cc/sec

$$V = \frac{n \, RT}{P}$$

$$V = \frac{(2.59 \times 10^{-7}) \; (8.2 \times 10^{-2}) \; (300)}{(1)} = 6.3714 \times 10^{-6} \, l/sec$$
$$\text{or}$$
$$6.3714 \times 10^{-3} \, cc/sec$$

4.   Using $\not{P} = \frac{8v \eta \, l}{\pi R^4 tp}$ we can calc. capillary requirement.

Set $\not{P}$ (that is ΔP in in. of H_2O) = $\sim$ 5" or $1.26 \times 10^4 \, \dfrac{dynes}{cm^2}$

$$v = 6.3714 \times 10^{-3} cc$$
$$t = 1 \; sec$$
$$\eta = 1.09 \times 10^{-4} \; poise$$
$$l = \text{solve for}$$
$$R = \text{set at } 0.0040"\, I.D.$$
$$p = 1 \; atmosphere$$

$$l = \frac{\pi R^4 tp \, \not{P}}{8v \eta} = 4.744 \; cm$$

5.   Similarly we arrived at a set of values for the fuels under

consideration and for the air and O_2 capillary flow meters.

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6.   Table

Fuel	Load	Capillary Required
CH_4	200 ma	$l = 4.744$ cm
C_2H_6		Bore = 0.0040" I.D.
C_3H_8 - -ΔC_3H_6		
C_4H_{10}	max of 2 Amps	ΔP range 1"$H_2O \rightarrow 3.7"H_8$
i-C_4H_{10}		

	Load	
C_2H_4	300 ma	$l = 4.744$ cm
C_3H_6		Bore = 0.0040" I.D.
C_4H_8	max 2 amps	$\Delta P_{Range} = 4.7"H_2O \rightarrow 2.3"H_8$

	Load	
CO	200 ma $\rightarrow$ 2 amps	7.83 cm = l
		Bore = 0.1110"I.D.
		$\Delta P = 0.95"H_2O \rightarrow 9.4"H_8$

	Total Range of Flow	
Air +/or O_2	$1.27 \times 10^{-2} \dfrac{cc}{sec} \rightarrow 3.2 \dfrac{cc}{sec}$	$l = 7083$ cm
		Bore = 0.011"I.D.
		P 1" $H_2O \rightarrow 9"H_8$

VII. APPENDIX C

PRECISION SYRINGE DRIVE CALIBRATIONS

Syringe Size	Gear #7 (cc/min)	Gear #8 (cc/min)	Gear #9 (cc/min)	Gear #10 (cc/min)	Gear #11 (cc/min)	Gear #12 (cc/min)
200	1.2	0.6	0.24	0.24	0.06	0.024
100	0.75	0.375	0.15	0.075	0.0375	0.015
50	0.46	0.229	0.092	0.046	0.023	0.009
20	0.23256	0.11628	0.046512	0.013256	0.011628	0.004653
10	0.1292	0.0646	0.02584	0.01292	0.00646	0.002585

All of above, except for 20 cc values, were determines by displacement of Hg over a timed interval.

VIII.   <u>REFERENCES</u>

1.   K. Kordesh and A. Marko, J. Electrochem. Soc. <u>107</u>, 480 (1960)

2.   L. W. Niedrach, Summary Report-Section #1 (Report Number 19), Contract #DA44-009-ENG-3771, U.S. Army ERDL, Nov. 1, 1959 to Nov. 30, 1961.

3.   A. D. Tevebaugh, E. J. Cairns, Final Technical Summary Report - Section II, Contract #Da-44-009-ENG-4853, ARPA Order Number 247-61, Dec. 1, 1961 - Dec. 31, 1962.

IX.   FIGURE CAPTIONS

Figure 1   -   Photograph of Teflon fuel cell and associated apparatus.

Figure 2   -   Photograph of disassembled fuel cell.

Figure 3   -   Teflon Electrolyte Chamber.

Figure 4   -   End plates containing gas chambers.

Figure 5   -   Stainless steel end plates.

Figure 6   -   Reservoir and adapter

Figure 7   -   Sampling elbow and inlet-and-outlet plugs.

Figure 8   -   Connector elbow, connector plug, and cell connector.

Figure 9   -   Circuit diagram for modified Kordesch-Marko interrupter.

Figure 10   -   Dual-range capillary tube flowmeter.

Figure 11   -   General view of fuel cell apparatus.

Figure 12   -   Schematic diagram of fuel cell apparatus.

Figure 13   -   Summary of life test data for $CH_3OH(Pt)/Cs_2CO_3/O_2$
                     (Pt) cell operated at 130^oC.

Figure 14   -   Initial current density-voltage curves for CH_3OH fuel
                     cell on life test.

Figure 15   -   Current density-voltage curves after 82 hours of
                     operation. An addition of electrolyte was made just
                     after these data were taken.

Figure 16   -   Current density-voltage curves after 162 hours of
                     operation.

Figure 17   -   Current density-voltage curves after 228 hours. All pre-
                     vious data and these were for operation on air-
                     saturated fuel.

IX. <u>FIGURE CAPTIONS</u> (Cont'd)

Figure 18   -   Current density-voltage curves after 324 hours. These data and all subsequent data were for operation on fuel prepared from boiled CH_3OH and H_2O

Figure 19   -   Current density-voltage curves after 374 hours. Comparison of performance using dry O_2 and 110 mm Hg of O_2+650 mm Hg of H_2O.

Figure 20   -   Current density-voltage curves after 563 hours. Cell operation discontinued after these data were taken.